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The use of raw and calcined diatomite in cement production

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Abstract

In this research, the use of raw and calcined diatomite which is in amorphous and porous nature was investigated in cement production. The physical, chemical, mineralogical, micro-structural and mechanical tests of the mortars, prepared by mixing Portland cement clinkers with 5%, 10% and 20% raw and calcined diatomite (w/w) and gypsum were carried out. According to the test results, raw diatomite blended cements have produced comparable strength values with respect to the reference cement (OPC) up to 10% addition; increased additions resulted in decreases in the strength due to the higher water demand related to the porosity while Blaine values and reactive SiO_2 content were increased. Calcination changed the porous structure of diatomite and eased the grindability as well as providing it to be used as a cement addition at a higher rate of 20%.

Keywords: Diatomite; Calcination; Blended cements

1. Introduction

Cement is an important building material whose production increases day by day. New cement products are developed according to the demands and for new construction technology; pozzolanic cements are especially becoming more common. Pozzolans are alumina–silicate bearing materials [1]. Cement industry utilize the pozzolans as natural (volcanic tuff, zeolite and diatomite) or synthetic forms. Synthetic pozzolans are produced from industrial wastes such as fly ash, silica fumes, slags or by applying heat treatment on clays (metakaolin). For the use of pozzolanic cements, apart from economical and environmental advantageous [2,3], their effects on reducing alkali aggregate reactions [4] and increasing strength against chemical media [5–9] are considered to be important. The insulation properties [10,11] and the weight of the structural materials [12–17] are now also very crucial. Diatomite is the only pozzolanic material which meets the required properties stated above [1]. As well known, diatomite is the fossil type of material which was formed by the accumulation of siliceous shells of algeas and it has a chemical formula of $SiO_2 \cdot nH_2O$ [18]. It can be found at higher purity or may contain various impurities at different rates such as sand, silt, clay, limestone, marn and tuff.

Diatomite is an important industrial ore with distinctive properties [19]. There are numerous publications on the properties and the use of diatomite [20,21]. Diatomite is mostly used for filtration. There are many reasons for the use of diatomite in filtration such as; its high porosity and bulk volume, its porous and permeable structure, its resistance to chemicals and high purity, large filtration surface area, its good adsorption properties especially for oils and micro-organisms [22]. Calcinated diatomite also provides higher flow rates in filtration. Because of these properties, diatomite is used as a filtrating material or as a constituent of a ceramic filter body, mainly for the filtration of sugar syrup, beer, whisky, wine, fruit juice, mineral or vegetable oils, pharmaceuticals and for the refining of waste water, dry cleaning solvents, industrial wastes, chemicals, varnishes [20,23,24]. It was recently proven that diatomite can also be added to cement as one of its constituents

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for improvement [25]. Diatomite is also chemically inert for most substances and has very low thermal conductivity [18].

Diatomite has been known as pozzolanic material since the ancient time. It is known that the dome of the Hagias Sophia in Istanbul (constructed in A.D. 500) was made using the diatomite based bricks due to weight advantage [18]. However, the research on the use of diatomite as cement additive has recently been popular. The studies using various diatomites from Greece, Hungary and Romania have proved that diatomite additions increased the strength of cements [25–28]. Stamatakis et al. [25] have determined that diatomites (from Greece, Hungary and Romania) with high silica content (75.00–77.68%) had reactive silica in between 50.50% and 69.07% while the diatomites with low silica content (30.25–59.90%) had reactive silica in between 25.50% and 45.02%. They have also reported that strength development was increased depending on the increased diatomite addition and reactive silica content. Moreover, Fragoulis et al. [26] found that diatomite addition due to reactive silica content played important role in strength development. In the other research with clayey and calcareous diatomite, it was concluded that reactive silica content and high Blaine values improved mechanical properties and therefore, diatomite could be used as a cement additive. However, it was recommended that it should be used with super-plasticizers because of the high water demand [27,28].

According to the related studies, the strength of the diatomite blended cements is decreased mainly due to the increased water demand which is limiting the use of diatomite as cement additive. However, if this problem is overcome, diatomite can be used as a valuable cement additive such as silica fumes since it contains reactive SiO_2. It is also a very important aggregate due to its light weight reducing the dead load of the constructions and high thermal insulation capacity [11,27]. At this point, it is believed that the problem limiting the use of diatomite as pozzolan can be overcome by changing the micro-structure by a heat treatment.

In this research, the use of raw and calcined diatomite of Kütahya/Alayunt region in Turkey, whose SiO_2 content varies between 50% and 90% with a possible reserve of 15 million tones [29], was investigated and the effects of diatomite addition to cement properties as pozzolan were tested.

2. Materials and methods

2.1. Materials

The raw materials used in this research were Portland cement clinker, diatomite and gypsum. Portland cement clinker and gypsum were obtained from Batı Söke Cement Factory (Aydın/Turkey). Diatomite was obtained from Kütahya/Alayunt (Turkey) region and was prepared as both raw and calcined forms. In preparation of the mortar specimens, standard aggregate whose properties are given in Table 1 (produced by SET Trakya Cement Factory) and tap water were used.

Table 1
Chemical and physical compositions of the standart aggregates used (wt.%)

Chemical composition	(%)	Sieve size (mm)	Cumulative over size (%)
SiO_2	94.05	2.0	–
Al_2O_3	2.98	1.6	6.65
Fe_2O_3	0.15	1.0	35.02
CaO	0.17	0.5	62.24
MgO	0.03	0.16	82.14
SO_3	0.05	0.08	99.01
K_2O	1.20		
Na_2O	0.85		
Humidity	0.11		
L.O.I.	0.57		

Table 2
Chemical compositions of the materials used (wt.%)

Oxides	Clinker	Gypsum	Diatomite (raw)	Diatomite (calcined)
SiO_2	20.50	0.38	78.24	93.60
Al_2O_3	5.25	0.02	0.55	0.95
Fe_2O_3	3.85	0.07	1.12	1.29
CaO	63.48	32.14	1.06	1.25
MgO	1.37	0.12	0.87	0.81
Na_2O	0.89	0.04	0.89	0.55
K_2O	0.40	0.02	0.75	0.46
SO_3	1.21	46.12	0.98	0.21
Free CaO	0.93	–	–	–
L.O.I.	0.42	21.02	15.54	0.51
Reactive SiO_2			62.33	71.21

Table 3
Mineralogical composition of the clinker (Bogue calculation) (wt.%)

Mineralogical phases	C_3S	C_2S	C_3A	C_4AF
Clinker	58.4	14.9	7.4	11.72

The clinker and gypsum specimens were first dried for 2 h and ground in a disc mill for 4 min and screened under 100 μm. The chemical analysis was then made using an ARL-8680$^+$ model X-ray spectrophotometer according to the Turkish Standard called TS EN 196-2.[1] The result of chemical analysis is given in Table 2 and the mineralogical composition of the clinker was calculated by the Bogue formulas as given in Table 3.

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[1] TS EN 196-1 Methods of testing cement-Part 1: Determination of strength.TS EN 196-2 Methods of testing cement-Part 2: Chemical analysis of cement.TS EN 196-3 Methods of testing cement-part 3: Determination of setting time and soundness.TS EN 196-5 Methods of testing cement-Part 5: Pozzolanicity test for pozzolanic cement.TS EN 196-6 Methods of testing cement;Part 6: Determination of fineness.

2.2. Methods

2.2.1. Preparation of diatomite

Preparation of diatomite was carried out at two stages in order to find out the pozzolanic effects of temperature. First, the diatomite samples were dried and ground and then the thermal behavior of raw diatomite was determined by a thermal analysis (first stage). Thermal analysis was carried out using a Perkin–Elmer-Diamond model STA instrument. Tests were carried out in a platen crucible and in an air atmosphere. The instrument was programmed so that it provided heating from 25 °C to 1000 °C by 20 °C/min rate and a stop for 1 h at 1000 °C and then a cooling from 1000 °C down to the room temperature by the same rate.

In the second stage, heat treatment (calcination) was applied to the samples according to the results of thermal analysis. Calcination of the diatomite samples was made using a Protherm-PLF 150/S model process controlled oven in air atmosphere since it was understood that there was no weight losses at 1000 °C according to the TG-DTA results. The process was so programmed that it created a heating up to 1000 °C by a rate 20 °C/min and a stop at 1000 °C for 1 h and then a cooling down to the room temperature by the same rate.

The chemical analysis and reactive SiO_2 tests of the raw and heat treated diatomite samples was made according to the Turkish Standard TS EN 196-2 Reactive SiO_2 test was performed with chemical processes by using hydrochloric acid (36% w/w) and potassium hydroxide (37% w/w). The results were summarized in Table 2.

For the tests, some physical properties of the pozzolanic materials and cement mixes were determined. For example, specific gravity of the samples was determined by using a Beckman 930 model picnometer, whereas specific surface area measurement was made by a Tonindustrie Seger model Blaine instrument. Particle size groups were obtained by using an Alpine Air Jet Sieves (A 200 LS model) and sieves of 45, 90, 200 μm according to the Turkish Standard TS EN 196-6. The results of the measurements are given in Table 4.

The mineralogical analysis of the raw and calcined diatomite samples were made using a Rikagu Miniflex brand ZD13113 series XRD instrument with Cu Kα rays ($\lambda = 1.54$ Å).

Micro-structural analysis of the diatomite samples was made using a Zeiss-Supra TM 50 VP model variable pressure analytical FESEM instrument. Raw and calcined diatomites were seen to be in similar shapes but in different sizes; irregular pore shapes were dominant in calcined diatomites.

Table 5
Compositions of the cement mixtures (wt.%)

Mixtures	Clinker	Gypsum	Raw diatomite	Calcined diatomite
Clinker–gypsum				
OPC	96.5	3.5		
Substitution of clinker–gypsum with raw diatomite				
5RD	91.5	3.5	5	
10RD	86.5	3.5	10	
20RD	76.5	3.5	20	
Substitution of clinker–gypsum with raw diatomite				
5CD	91.5	3.5		5
10CD	86.5	3.5		10
20CD	76.5	3.5		20

2.2.2. Preparation of reference and blended cements

The cements used in the tests were grouped as reference, raw diatomite and calcined diatomite blended cements. Reference cement was obtained by adding 3.5% gypsum to the Clinker by weight and is called OPC. Raw diatomite blended cement specimens were obtained by replacing the Clinker with raw diatomite at various rates (5%, 10% and 20%) by weight and keeping the gypsum at 3.5% in the composition, as clearly seen in Table 5. These samples were called 5RD, 10RD and 20RD, respectively. Similarly, calcined diatomite blended cement specimens were obtained by replacing the Clinker with calcined diatomite at various rates (5%, 10% and 20%) by weight and keeping the gypsum at 3.5% in the composition (Table 5). These samples were called 5CD, 10CD and 20CD, respectively.

Reference and diatomite blended cement samples were ground in a laboratory type of ball mill for 30 min. The chemical and physical properties of the samples were determined according to the Turkish Standards called TS EN 196-2 and TS EN 196-6, respectively (Tables 6 and 7).

2.2.3. Preparation of mortars

Mortars were prepared in a mixer according to TS EN 196-1 which specifies 450 g cement, 1350 g standard aggregate (Table 1) and 225 mL water for each mixture. At this stage, standard water demand, soundness and setting time tests were made on the fresh mortar samples according to the TS EN 196-3. Setting time and water demand tests were made using a Vicat instrument called RMU 24100 Bergamo Viq Gremello 57 model (room temperature was

Table 4
Particle size distribution

Material	Range dimension			Blaine (cm^2/g)	Specific gravity (g/cm^3)
	>45 (μm)	>90 (μm)	>200 (μm)		
Raw diatomite	8.2	5.5	0.1	5430	2.54
Calcined diatomite	16.5	11.7	0.2	4100	2.52

Blaine and specific gravity of diatomite samples (wt.%).

Table 6
Chemical compositions of the cement mixtures (wt.%)

Mixtures	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	L.O.I.
OPC	19.24	5.56	2.84	62.48	2.40	0.40	0.91	2.61	2.79
5RD	22.07	5.26	2.69	59.60	2.29	0.11	0.88	2.60	3.47
10RD	22.47	5.13	2.71	60.03	2.17	0.09	0.89	2.57	3.53
20RD	31.21	4.97	2.48	50.08	2.25	0.10	0.79	2.15	3.66
5CD	22.53	5.36	2.68	59.18	2.34	0.10	0.87	2.57	3.24
10CD	26.07	5.06	2.58	56.07	2.23	0.08	0.85	2.44	3.09
20CD	33.60	4.86	2.49	50.18	2.21	0.11	0.79	2.10	2.77

Table 7
Physical properties of the cement mixtures (wt.%)

Mixtures	Range dimension			Blaine (cm^2/g)	Specific gravity (g/cm^3)
	>45 (μm)	>90 (μm)	>200 (μm)		
Clinker–gypsum					
OPC	20.3	4.7	0.8	3247	3.15
Substitution of clinker–gypsum with raw diatomite					
5RD	14.2	0.7	0.5	4182	3.04
10RD	12.8	0.8	0.4	4861	2.99
20RD	11.9	1.8	0.1	6045	2.88
Substitution of clinker–gypsum with calcined diatomite					
5CD	10.2	0.8	0.0	3940	3.05
10CD	10.8	1.1	0.0	4396	3.00
20CD	12.0	1.7	0.0	4920	2.89

20 °C and relative humidity was 50–60%). Soundness tests were made on a brass Atom Teknik Le-Chatelier instrument (Table 8).

For the flexural and compressive strength tests, the mortar samples were placed in rectangular moulds having a size of 40 × 40 × 160 mm. The mortars in the moulds were vibrated for 1 min for a better placement and then kept in the moulds for 24 h at room temperature. After that, they were taken off the moulds and placed in a curing bath at 20 °C. They were taken from the curing bath after 2 days, 7 days and 28 days and dried for compressive and flexural strength tests. The tests were done according to TS EN 196-1 and using a Toni Technik brand hydraulic press. The result of the strength tests and micro-structural analysis of 20% raw and calcined diatomite blended mortars after 14 days.

3. Results and discussion

3.1. Thermal analysis

The changes occurred in diatomite after heat treatment can be seen from TG-DTA analysis (Fig. 1). From the DTA curves, the surface and hygroscopic water removal was seen as endothermic pattern in the heating stage; transition from amorphous to crystallized form was seen as a weak exothermic pattern in cooling stage. From the TG curve, it is seen that diatomite lost 6% surface humidity at 100 °C. With the increase of temperature, weight loss continued up to 980 °C and 8.5% weight loss was occurred due to the degradation of Montmorillonite and Opal-A. The weight did not change at 1000 °C for 1 h duration. After this period, a weight loss of 1.1% was observed with

Table 8
Water demand setting times and soundness of the cement mixtures

Mixtures	Water demand (wt.%)	Setting time (min)		Soundness (mm)
		Initial	Final	
Clinker–gypsum				
OPC	28.4	180	225	2
Substitution of clinker–gypsum with raw diatomite				
5RD	30.2	165	195	1
10RD	30.8	170	210	1
20RD	37.0	165	210	1
Substitution of clinker–gypsum with calcined diatomite				
5CD	31.2	180	225	1
10CD	32.2	175	225	1
20CD	37.4	160	210	1

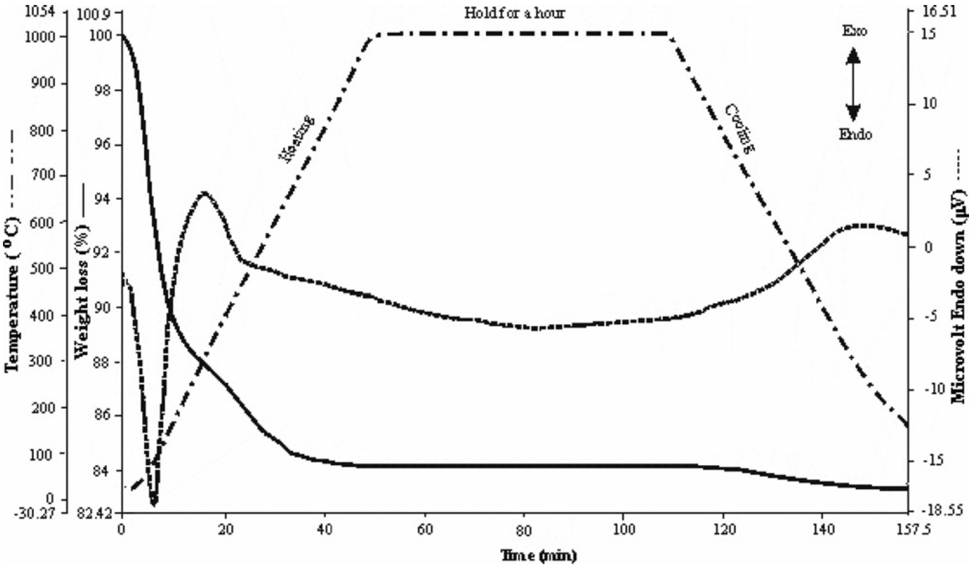

Fig. 1. Thermal analysis (TG-DTA) of the diatomite samples.

a weak exothermic reaction in the cooling stage and occurrence of Cristobalite proved that stronger crystal bonds were established.

3.2. Chemical analysis

According to the chemical analysis of the raw and calcined diatomite samples (Table 2), the amount of SiO_2, Al_2O_3 and Fe_2O_3 having pozzolanic properties were increased after calcination, whereas Na_2O, K_2O, SO_3 were decreased which increase the tendency for alkali aggregate reactions. The sum of SiO_2, Fe_2O_3 and Al_2O_3 are accounted more than 70% of the total raw and calcined diatomite. While the reactive SiO_2 percentage of the raw diatomite was 62.3, it increased up to 75.30% after calcination process. The rate of reactive SiO_2/total SiO_2 in raw diatomite was 76.9%, however, this rate was reduced to 76.1% while total SiO_2 increased. This was explained by transition from an amorphous form to a partly crystal form after heat treatment.

3.3. Mineralogical analysis

In the XRD diagrams of the raw and calcined diatomites (Fig. 2), extensive amorphous structure was seen in sections between 19° and 32° of 2-theta. In the amorphous section of raw diatomite Albite, Calcite and Opal-A peaks were noticed. Crystallized section was comprised of Montmorillonite and calcium magnesium silicate. Raw diatomite is mainly comprised of cation groups, namely CaO, and it exists in the structure of Montmorillonite and calcium magnesium silicate. MgO was the main constituents of calcium magnesium silicate. Na_2O and K_2O exist in Albite and Montmorillonite compositions. SO_3 and Fe_2O_3 were found as impurities in the compositions (Table 1). SiO_2 which is the body builder of raw diatomite was found to be in amorphous structure as Opal-A mineral.

In the amorphous section of the calcined diatomite, there were Anorthite, Cristobalite and Quartz peaks. After the calcination, aluminum silicate within the Albite and Montmorillonite were reacted with CaO and SiO_2 to produce Anorthite. Opal-A was converted to Quartz and Cristobalite.

When XRD results of both samples were compared, it was seen that raw diatomite had irregular structure and heat treatment made the structure more regular.

3.4. Micro-structural analysis

Microscopic structure of the diatomite samples were examined using the SEM pictures. Raw (Fig. 3) and calcined diatomites (Fig. 4) were seen to be in similar shapes such as cylindrical, spherical etc. but in different size. While variations were observed in raw diatomite structure, more irregular shapes were dominant in the calcined diatomites. The size of the shapes was in 5–10 µm.

Micro-structure of raw and calcined diatomite blended pastes was investigated through SEM pictures after 14 days of hydration. Acicular (needle-like) type of CH crystals (calcium hydroxide) developed both on the CSH (calcium silicate hydrate) and in the pores together with CSH coating developed on the hydrated cement grains in the micro-structure of 20% raw diatomite containing cement pastes were found (Fig. 5). There are pores of 5 µm in diameter between the hydrated grains in the structure. Moreover, there are $CA\bar{S}H$ (ettringite) crystals having hexagonal prism geometry developed in the pores together with CSH's. CSH over the hydrated cement grains within the micro-structure of cement pastes containing 20% calcined diatomite was developed as small and irregular pieces (Fig. 6). There are considerable amount of gel pores over the CSH

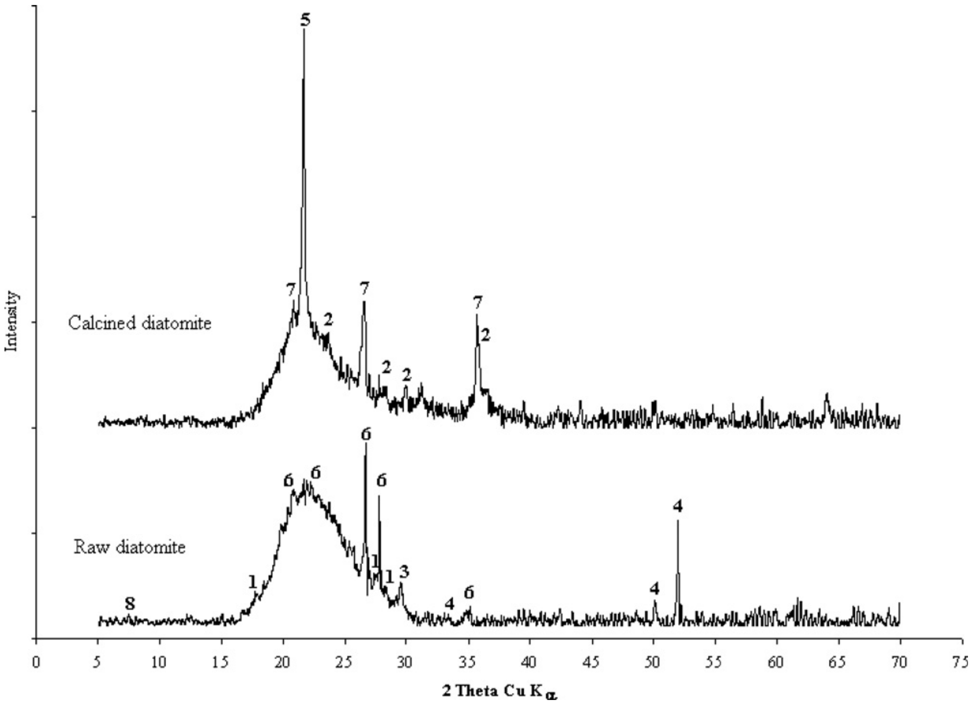

Fig. 2. X-ray diffraction patterns of raw diatomite before heating (25 °C) and after heating at 1000 °C temperatures for 2 hours (1: Albite 2: Anorthite 3: Calcite, 4: Calcium, Magnesium, Aluminum Oxide-Silicate, 5: Cristobalite, 6: Opal-A, 7: Quartz 8: Montmorillonite).

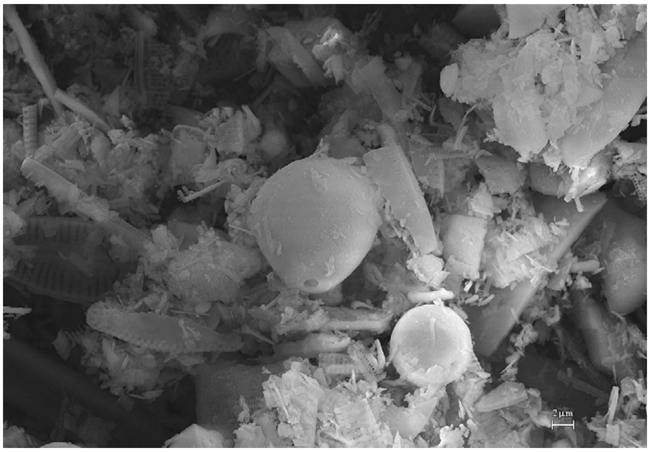

Fig. 3. SEM image of the raw diatomite.

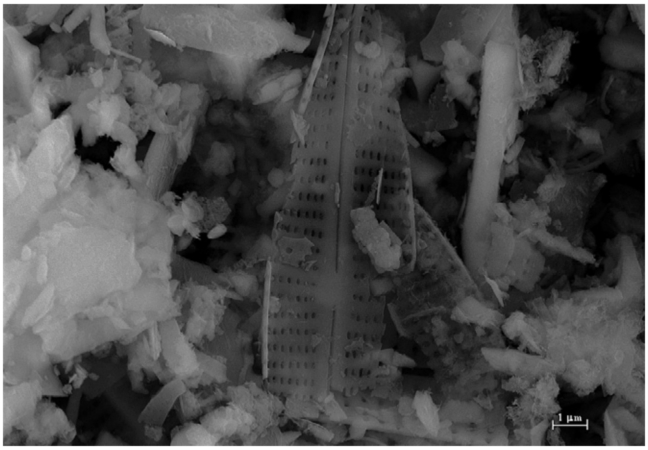

Fig. 4. SEM image of the calcined diatomite.

coating. Crystallized acicular type of CH and $CA\overline{S}H$ between the CH's were seen either over the CSH or in the pores. Porous structure was not clear due to the complex structure occurred. The reason for that can be explained by the occurrence of more compact structure with low Blaine values due to the crystallization from an amorphous structure after the calcinations.

3.5. Specific gravity

The most important feature of diatomite is its high porosity and low specific gravity. Specific gravity of the calcined diatomite was reduced to 2.52 g/cm^3 while it was 2.54 g/cm^3 in raw diatomite (Table 4). However, there was a different situation in the raw and calcined blended cements (Table 7) i.e. the specific gravity of the calcined diatomite blended cements were higher. This can be explained by the granulization of diatomite after calcination and accumulation of cement particles around these granules hence become a more compact form.

3.6. Fineness

Fineness result of the raw diatomite shows similarity with the literature [25–28]. Fineness of the diatomites increased after calcination (Table 4). The result that produced reduced Blaine values and increased over sieve values can be explained by the granulization. It was seen

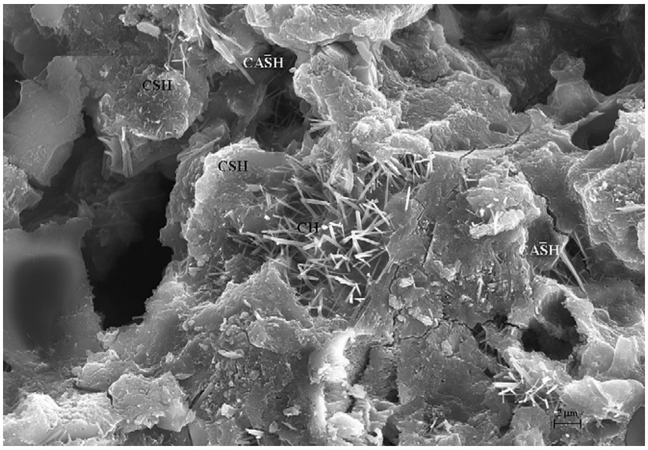

Fig. 5. SEM image of blended cement paste including 20% raw diatomite (after 14 days of hydration).

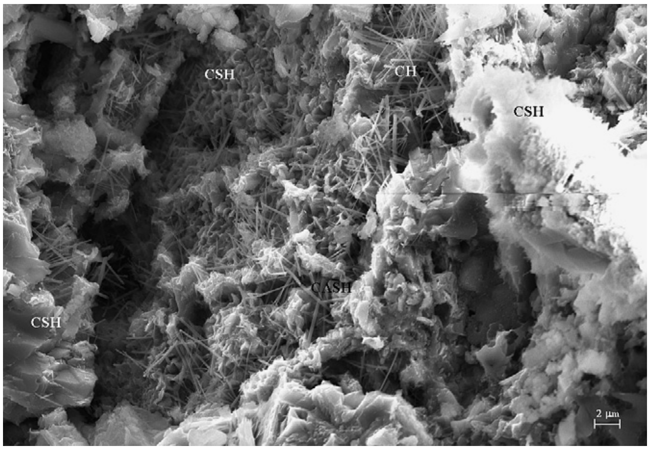

Fig. 6. SEM image of blended cement paste including 20% calcined diatomite (after 14 days of hydration).

that calcined diatomite blended cement had smaller particle size after grinding (Table 7). This was explained by the modification of the bonding structure after calcination and by the increase in brittleness with granulization which eased the milling together with clinker and gypsum to produce finer particles.

3.7. Specific surface area (Blaine)

The grindability of OPC, raw diatomite blended cements and calcined diatomite blended cements are different. It is easily seen that, under normal conditions, raw diatomite is grinded finer (5430 cm^2/g) than both calcined diatomite (4100 cm^2/g) and OPC (3247 cm^2/g). However, it was noticed that calcined diatomite eased the grindability although the decrease in Blaine value.

Raw diatomite addition in cement increased the fineness. The Blaine values as well as the other physical properties were affected by heat treatment. While particle size was increased after heat treatment and granulization, the Blaine values were reduced (Table 4). The reason for that can be explained by the occurrence of micro-structural form during granulization after calcinations. This situation is partly seen in the SEM images of calcined diatomite (Fig. 4) and clearly seen in the SEM images of the cement pastes (Fig. 6). It was also seen that fineness of the diatomite blended cements was increased, directly proportional to the diatomite addition if the other conditions were kept constant. When over sieve values were considered, it could be concluded that diatomite addition both in raw and calcined forms eased the grindability in the mill (Table 7).

3.8. Soundness (Le-Chatelier)

CaO, MgO and SO_3 constituents of cements cause soundness effects in the concretes produced by these cements [1]. Therefore, it is desired to have such constituents of cement as low as required. It is expected to have a lower soundness rate since such constituents decrease with increasing diatomite amount in the blend (Table 6). The results also supported this idea as seen in Table 8. It can be concluded that both raw and calcined diatomite addition to cement can increase the volume stability of the concrete to be produced by using diatomite blended cements.

3.9. Water demand

Water demand changes according to the chemical structure, specific surface area and porosity of the cement mixtures [1]. In blended cements, the fineness increases with addition rate (Table 7) which affects water demand. In fact, it was seen that water demand increased in all blending rates and Blaine values for the diatomite blended cement samples (Table 8). Setting time was not negatively affected as expected with increased water demand. This was explained by the water adsorption by the pores due to the high Blaine values. Although Blaine values in calcined diatomite are smaller than raw diatomite, the water demand did not change. In this case, it may be considered that calcined diatomite used the water available for hydration.

3.10. Setting time

Setting time of cements changes with particle size, specific surface area and mineralogical structure of the cement mixtures [1]. Raw and calcined blended cements had lower setting time than OPC (Table 8). In blended cements C_3A content decreases while the amount of gypsum remains constant. Although it is expected that setting time increases with pozzolan addition, setting time of the raw diatomite blended cements were found to be smaller than both calcined diatomite blended cement and OPC. The reason for this result is related to the diffusion controlled by hydration reactions in pozzolanic cements [30]. In fact, higher porosity of raw diatomite with high Blaine values eased the diffusion of water and increased solution of C_3A which in

Table 9
Compressive and flexural strength test results of the cement mortars

Mortars	Compressive strength (N/mm^2)			Flexural strength (N/mm^2)		
	2 days	7 days	28 days	2 days	7 days	28 days
Clinker–gypsum						
OPC	22.4	37.3	48.5	3.8	6.3	7.8
Substitution of clinker–gypsum with raw diatomite						
5RD	22.3	35.9	47.1	4.2	5.2	7.8
10RD	22.8	36.7	47.9	4.2	6.3	7.7
20RD	15.1	26.0	33.8	3.3	4.2	6.5
Substitution of clinker–gypsum with calcined diatomite						
5CD	22.0	35.0	47.5	4.0	6.0	7.7
10CD	22.3	34.3	49.2	3.7	6.2	7.9
20CD	19.3	33.6	48.2	3.8	5.8	8.1

turn increased the solubility of Ca^{2+} ions. Hence, the crystallization speed of CSH increased and setting time was shortened.

In calcined diatomite, setting time was shortened with increasing rate of addition since water diffusion became slower due to the decrease in Blaine value which caused slower C_3A solution and hence setting time prolonged.

3.11. Flexural and compressive strength

Since the strength of cement is a function of hydrated part, strength development is affected by mineralogical features of the clinker, pozzolanic reactions, Blaine, reactive SiO_2 ratio and water demand of the cement mixtures. Clinker phases which affect the strength values are seen in Table 2 and strength values were changed with the change in mineralogical phases due to increasing diatomite addition. Since the mineralogical structure of diatomite was changed by heat treatment, pozzolanic reactions and strength values depending on increasing rate of addition in cement mixtures were also affected. With pozzolanic reactions, Si–O tetrahedrals in diatomite structure tend to bind positive ions to stabilize due to electrovalence instability just like in zeolites [31] and they create CSH structure binding the CH group in the environment.

It was understood that early strength of the cements at 5% and 10% raw and calcined diatomite additions was a function of Blaine value. Early strength (2 days) of 5% and 10% raw and calcined diatomite blended cements was found to be close to that of OPC (Table 9). This result is in good agreement with the literature findings [25,26,32]. While 10% diatomite blended cement mixtures shown higher strength values, they were reduced when addition rate exceeded 10% mainly because of the voids caused by absorbed water. Early strength values were reduced in 20% diatomite blended cements although Blaine value was increased since porous structure of diatomite absorbs more water [33]. Similar results were seen in 7 days and 28 days strength values of raw diatomite blended cements.

When raw diatomite addition rate increased over 10%, strength values were decreased depending on the increased specific surface area and water demand. However, strength values were found to be closer to those of OPC when 20% calcined diatomite was added to the cement. In microstructural analysis after 14 days hydration, voids were observed in raw diatomite blended cements due to existence of adsorbed water and the pore structure (Fig. 5). A more compact structure was seen in calcined diatomite blended cement (Fig. 6). Calcined diatomite blended cements with lower Blaine values used up the water for hydration instead of adsorbing it into its porous structure although both had similar water demands. Strength test results are in good agreement with the other test (chemical, physical and micro-structure) results and flexural strength values were developed similar to the compressive strength values.

4. Conclusion and recommendation

Firstly, raw diatomite addition to cement up to 10% produced positive results. After 10% addition, strength values were reduced mainly because of the increased water adsorption of diatomite. This result has a common base with the other research findings on the use of diatomites as cement additive. However, calcination treatment was proven to be a good alternative for reducing water adsorption of diatomite and hence improving the mechanical properties of the diatomite blended cement mixtures. For this point of view, the results of this research will play a crucial role in developing cement based light construction materials. The other results of the research can be given as follows:

- Diatomite was converted to a more regular structure after calcination. After this conversion, average particle sizes and reactive SiO_2 rates were increased whereas, specific gravity and Blaine values were decreased. These physical and chemical changes in the property affected the pozzolanic features of the diatomite used.
- The grindability of raw and calcined diatomite are different. Under normal conditions, raw diatomite are grinded more easily, however, calcined diatomite eased the grinding when milled together with clinker. This fact can provide considerable energy saving in the milling operations of cement production.

- Diatomite addition to cement increases SiO_2 and reduces Na_2O and K_2O contents which may chemically enable the production of more durable concretes.
- Diatomite is known as a pozzolanic material having high amount of natural reactive SiO_2 in the composition which is further increased by calcination.
- The specific gravity of diatomite is 20% lower than that of Portland cement which enables the production of lighter structural concrete components using diatomite blended cements.
- Diatomite addition to cement decreases the soundness causing constituents in the composition which will provide better volume stability for the concrete.
- Setting time of the pozzolanic cement mortars will be reduced due to porosity of diatomite and diffusion of water affecting the solubility of clinker constituents. Setting time of the mortars can be arranged using regulating additives.
- Strength values will be reduced since the amount of water to be adsorbed is increased due to higher Blaine values depending on raw diatomite porosity. However, mechanical performance of concrete produced by using calcined diatomite blended cements will be improved since calcination produces granular diatomite with lower Blaine values.
- Early (initial) strength values are increased by the addition of both raw and calcined diatomite up to 10% addition rate. As a cement addition, raw diatomite can be used up to 10% and calcined diatomite can be used up to 20%. However, if raw diatomite is used, it should be noted that this can only produce low strength standard cement in the early stage and therefore, the concrete design should be made accordingly.
- When 28 days strength values are considered, it was seen that 20% raw diatomite blended cements required longer curing time than calcined diatomite blended cements and OPC.

It is recommended that more research should be done on reducing water adsorption capacity related to the pore structure of diatomites.

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