Available online at www.sciencedirect.com

ScienceDirect

Cement & Concrete Composites 30 (2008) 194–201

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Studies on cement and mortar containing low-calcium fly ash, limestone, and dolomitic limestone

Bülent Yılmaz [a], Asim Olgun [b,*]

[a] Department of Ceramic Engineering, Dumlupinar University, Kütahya, Turkey
[b] Department of Chemistry, Dumlupinar University, 43100 Kütahya, Turkey

Received 20 June 2006; received in revised form 11 July 2007; accepted 25 July 2007
Available online 3 August 2007

Abstract

The effects of low-calcium fly ash (FA), limestone (LS), and dolomitic limestone (DLS) on the properties of cement and mortar has been investigated through a number of tests. Composition of cement hydration products in cement paste and mortar were made with clinker (PC), gypsum (G), FA, LS and DLS. The binders employed were Portland cement (OPC), fly ash–portland cement (FA–OPC), FA–LS–OPC, and FA–DLS–OPC blends with a maximum PC replacement level of 40%, FA level of up to 40%, LS and DLS levels of up to 15%. The hydration rate and products were studied by means of X-ray diffraction (XRD) and Fourier transforms infrared spectroscopy (FTIR). The results showed that the FA, LS and DLS prolong the setting time of the cements. Relative to OPC, in FA–OPC system expansion decreases as the fly ash content of the cement increases. Ternary system, FA–DLS–OPC produces a marked fall in the expansion of the tested specimens.

Keywords: Expansion; Fly ash; Limestone cement; Dolomite; Strength

1. Introduction

The use of replacement materials such as fly ash and limestone in Portland cement has been gaining much attention in recent years [1–5]. Fly ash improves concrete properties, lowers the costs of concrete production, and is ecologically beneficial. The utilization of fly ash is one of the popular methods proposed to reduce expansion due to alkali–silica reactivity. However, its behavior is not completely understood. Several points are relevant regarding its effect on the expansion of concrete. According to Shehata and Thomas [3], chemical composition may be used to provide an indication of performance of fly ash in concrete. The expansion of concrete increases with increasing calcium oxide or alkali content of fly ash and decreases as its silica content increases. Several studies also reported that the fly ash is effective at reducing the amount of alkali ions available in the pore solution for reaction with potentially reactive aggregates, which result to a decrease in the expansion of concrete [3,6].

In the present study, since the incorporation of fly ash in cement paste and concrete can reduce expansion due to alkali–silica reactivity, efforts have been made to use fly ash in the production of Portland–limestone cement and Portland–dolomitic limestone cement. Previous studies have shown that cement containing limestone exhibit higher early compressive strength compared to that of ordinary Portland cement [5]. However, care must be taken to control the expansion due to the reactions that take place between limestone, dolomitic limestone and Portland cement [7].

This paper examines the influence of combined action of OPC + FA, OPC + FA + LS, and OPC + FA + DLS on the properties of cement. The present work has systematically studied the influence of increasing FA addition (5–40%), LS (5–15%), and DLS (5–15%) on physical and mechanical properties of cement and composite cements. Data obtained using X-ray diffraction and

---

[*] Corresponding author. Tel.: +90 274 2652051; fax.: +90 274 2652056.
E-mail address: aolgun@dumlupinar.edu.tr (A. Olgun).

0958-9465/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2007.07.002

scanning electron microscopy (SEM) to study the hydration products of these three composite cement are compared with similar data from a control sample, based on the same Portland cement paste.

2. Experimental procedures

2.1. Materials

The cementitious materials used in this study were Portland cement clinker (PC), coal fly ash, limestone and dolomitic limestone. The chemical composition of all materials is given in Table 1. The PC, limestone, and gypsum come from Çimsa cement Plant (Mersin, Turkey) and dolomitic Limestone from Kümaş Plant (Kütahya, Turkey). The fly ash was obtained from Iskenderun Thermal Power Plant (Iskenderun,Turkey) The fly ash meets general requirements of ASTM class F and has a relatively low CaO content of 3.8%.

2.2. Cement mixtures

Three series of mixtures and one reference mixture were prepared according to TS EN 197-1 [8]. Before mixing, gypsum optimization was done for the clinker used and was found to be 5 wt.% of the clinker. Reference mixture has been produced by intergrinding PC and gypsum, and designated as R. The other series of mixtures were designated as FA(FA + G + PC), LS(FA + G + PC + LS), and DLS(FA + G + PC + DLS). The details of mixtures as well as their chemical compositions are given in Table 2. A laboratory ball-mill was used for the grinding process. The physical tests were carried out following grinding according to TS EN 196–6 [8]. Particles analysis was done by using Alpine sieves with 45-, and 90-μm size sieves. The fineness of the mixtures was between 3100 and 4320 of Blain's specific surface.

Table 1
Chemical composition of materials (%)

Oxide	Clinker	Gypsum	Fly ash	Limestone	Dolomitic limestone
SiO$_2$	20.89	2.4	56	2.58	2.47
Al$_2$O$_3$	5.68	0.71	22.5	0.68	0.84
Fe$_2$O$_3$	3.08	0.35	6.8	0.33	0.34
CaO	65.6	32.3	3.8	52.39	31.5
MgO	2.28	0.38	2.3	0.64	19.12
SO$_3$	1.12	42.8	0.25	0.1	–
K$_2$O	0.95	0.1	1.9	0.11	0.09
Na$_2$O	0.32	0.08	0.85	–	0.11
L.O.I.	0.1	20.95	2.4	41.88	45.37

2.3. Testing procedure

The required water of standard consistency and setting time and volume expansion were examined according to TS-EN 196-3 [8]. The mixing of cement pastes was carried out with the standard water of consistency as given in the Table 2. The cement pastes were obtained using a mixer for 1 min at low speed (60 rpm) and 4 min at high speed (120 rpm). The paste was then poured into moulds creating 100 × 10 × 10 mm prisms. The samples were cured at 20 ± 2 °C and 90 ± 2% relative humidity. The samples were then demolded and placed in deionized water. The cement paste specimens were cured for 2, 7, and 28 days, and then they were taken out of the water. The hydration process was stopped by grinding the hydrated samples with acetone and by washing the residue several times with more acetone. The samples were dried at 65 °C.

A piece of hydrated cement paste prism was taken and was ground to a fine powder of <63 μm. A Rikagu Miniflex X-ray diffractometer using mono-chromatic CuKα radiation operating at a voltage of 30 kV and current of 15 mA was used. A scanning speed of 2° 2θ/min and a step size of 0.02° were used to examine the samples in the range of 5–60° 2θ.

For scanning electron microscopy studies, selected cement paste samples cured for 14 days were used. A cement prism was cut into cubes ≈10 mm square, one side of which was ground flat. The hydrated samples were flooded with acetone to stop hydration reactions. After drying and coating with gold the SEM image of samples were obtained using a ZEISS SUPRA 55VP FESEM scanning electron microscope.

Table 2
Physical characteristics of cementitious mixes

Symbol	Cement mixes	Water demand (%)	Fineness (wt.%)		Specific surface (cm^2/g)	Density (g/cm^3)
			+45 μ	+90 μ		
P	5% G + 95% PC	28.3	7.9	0.5	3570	3.13
FA$_1$	5% G + 5% FA + 90% PC	27.8	8.2	0.7	3550	3.09
FA$_2$	5% G + 10% FA + 85% PC	27.6	8.6	0.8	3520	3.05
FA$_3$	5% G + 20% FA + 75% PC	27.4	9.3	1.1	3480	2.97
FA$_4$	5% G + 40% FA + 55% PC	27.2	10.7	1.8	3380	2.81
LS$_1$	5% G + 15% FA + %5 LS + 75% PC	27.9	9.7	1.3	3535	2.99
LS$_2$	5% G + 10% FA + %10 LS + 75% PC	28.1	10.1	1.4	3600	3.01
LS$_3$	5% G + 5% FA + %15 LS + 75% PC	28.1	10.5	1.6	3660	3.03
DLS$_1$	5% G + 15% FA + %5 DLS + 75% PC	26.5	9.7	1.2	3500	2.99
DLS$_2$	5% G + 10% FA + %10 DLS + 75% PC	26.6	10.2	1.2	3520	3.02
DLS$_3$	5% G + 5% FA + %15 DLS + 75% PC	26.5	10.6	1.2	3545	3.04

The FT-IR spectra of hydrated Portland cement and composite cement pastes were recorded on a Bruker Vertex 70 FT-IR spectrometer equipped with the harric MVP2-unit in the range of 4000–400 cm^{-1} region.

The specimen preparation for strength tests was performed at the room temperature. Mortar specimens were produced by mixing one part of the cement with three parts of sand, using a water-to-cement ratio (w/c) of 0.50. The cement–water mixtures were stirred at low speed for 30 s, and then, with the addition of sand, the mixtures were stirred for 4 min. The mortars prepared were cast into 40 × 40 × 160 mm moulds for strength tests. After 24 h of curing at 20 °C, the samples were demolded, and then immediately immersed in a water-curing tank. The temperature of the water was maintained at 20 ± 1 °C during the curing period. The compressive strength test was carried out at the ages of 2, 7, 28 days according to TS EN 196-1 [8].

3. Results and discussion

3.1. Compressive strength

The compressive strength of each batch at a particular age was an average of three tests. The comparison of strength of the mortar containing fly ash with control mortar containing Portland cement is shown in Fig. 1. All batches of fly ash mortar had lower strengths than the control at the ages of 2, 7, and 28 days. For fly ash mortar, the higher the replacement level, the more notable the reducing effect on the compressive strength of the specimens. The decrease in the strength of the mortar due to addition of fly ash can be attributed to the pozzolanic activity of the fly ash. Cyr et al. [9] found that pozzolanic reaction of the fly ash is slow and depending on the amount and solubility of amorphous silica in the material, a long curing period is needed to observe its positive effects.

The strength development of the tested composite cement mortar is illustrated in Figs. 2 and 3. In this investigation, an attempt was made to establish whether a suitable combination of a fly ash and limestone, and fly ash and dolomitic limestone in cement would improve the early strength of the mortar more than fly ash would separately. Therefore, the optimum level of fly ash in cement was taken as 20 wt.% of PC and the fly ash was replaced with the limestone and dolomitic limestone up to a level of 15% weight of cement. It is observed that incorporation of fly ash and limestone, and fly ash and dolomitic limestone resulted in an increase in 2-day compressive strength compared to the strength of the mortar containing 20% fly ash. The increase in the early strength of the mortar due to the addition of limestone and dolomitic limestone can be attributed to their active participation in cement hydration and filler effect of the fine particles of limestone and dolomitic limestone [5,10]. The additional surface area provided by the limestone particles may provide sites for the nucleation and growth of hydration products that leads to further increase in strength [10,11]. It was also observed that the relative increase in the strength of the mortars between 7 and 28-days became smaller at higher content of limestone and dolomitic limestone. Results show that combined action of FA and LS has more pronounced positive effect

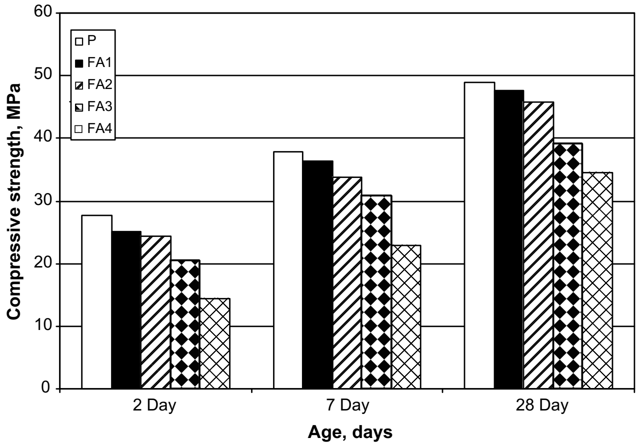

Fig. 1. Compressive strength of the mortar containing fly ash.

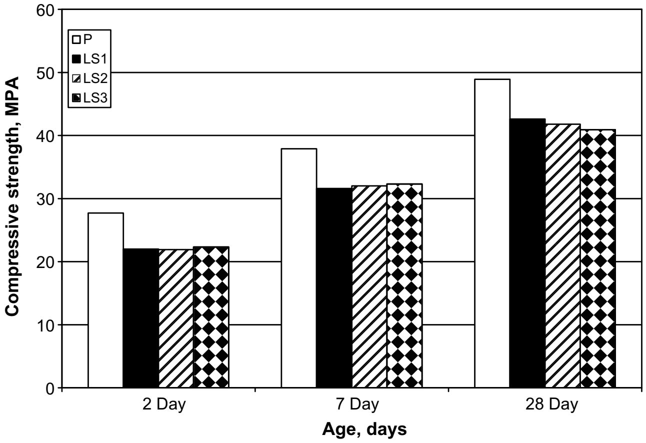

Fig. 2. Compressive strength of the mortar containing fly ash and limestone.

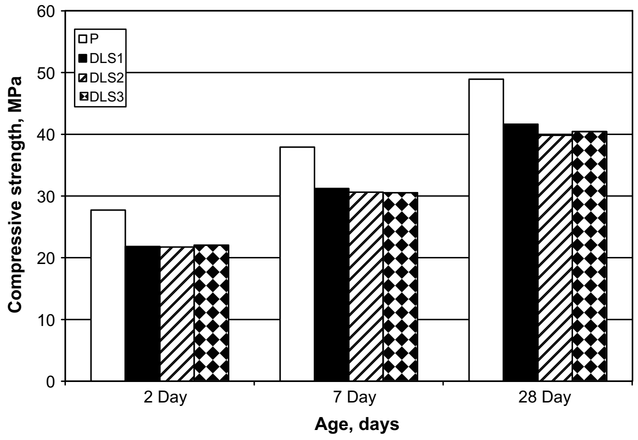

Fig. 3. Compressive strength of the mortar containing fly ash and dolomitic limestone.

on the compressive strength compared to the mortar containing FA and DLS.

3.2. Water demand, setting time, and soundness

Table 2 shows the test results from the determination of water-percent, volume expansion (according to Le Chatelier process), and setting time for cement mixes. Large amount of fly ash addition slightly decreased the water demand of the cement paste. Although water to cement ratio values required to obtain normal consistency were similar for Portland cement, they ranged from 28.3% to 27.4%. The effect of fly ash on the paste water demand of cement can be attributed to the fineness of fly ash [12]. The limestone cement, despite their higher fineness, generally demands less water than the corresponding pure cement. This is due to different particle size distribution of limestone cement [13]. Dolomitic limestone cement was generally coarser than Portland and limestone cement according to percent value of 45-µm and 90-µm sieve residue. Therefore, the water requirement was low in dolomitic limestone cement.

Table 3
Physical properties of cementitious mixes

Symbol	Setting time (min)		Expansion (Le Chatelier) (mm)
	Initial	Final	
P	145	170	2
FA_1	145	165	1.5
FA_2	155	175	2
FA_3	170	190	1.5
FA_4	190	220	1
LS_1	165	205	1.5
LS_2	165	195	1
LS_3	150	185	1.5
DLS_1	185	235	1
DLS_2	185	225	0.5
DLS_3	180	210	1.5

From the setting time data in Table 2, it is clear that the use of fly ash in cement resulted in a prolonged initial and final setting time with respect to corresponding Portland cement. The observed retardation in setting time may be attributed to the small pozzolanic contribution of fly ash. These results are in good agreement with those reported by Kula et al. [12]. The initial and final setting time of the cement was further prolonged as the FA + DLS was introduced in the matrix. The observed retardation in setting time mainly can be attributed to the MgO content of dolomitic limestone cement. Dolomitic limestone cement has relatively higher MgO content than the other cement mixes. These results comply with an earlier study of Zheng et al. [14].

The effects of replacement materials on the volume expansion of cement paste are shown in Table 3. The results indicate that the replacement of FA by PC reduces expansion compared to control cement paste without fly ash. Moreover, there is a slight decrease in the expansion as the fly ash content increases ranging from 5% to 40%. This behavior is typical of the other low-calcium fly ashes used in the earlier study and reported elsewhere [3]. The decrease in the expansion may be attributed to the CaO content of the fly ash. It was reported that fly ash with low alkali and CaO content is effective at reducing the expansion of concrete due to alkali–silica reaction [3]. The soundness of the LS cement and DLS cements is satisfactory; the expansion measured varies from 0.5 mm to 1.5 mm while the limit according to TS EN 197-1 is 10 mm. It is interesting to note that the expansion of DLS cement was relatively smaller than that of the LS cement.

3.3. Hydration of Portland cements

The development with time of the four cement systems, as indicated by XRD, is shown in Figs. 4–6. They show the

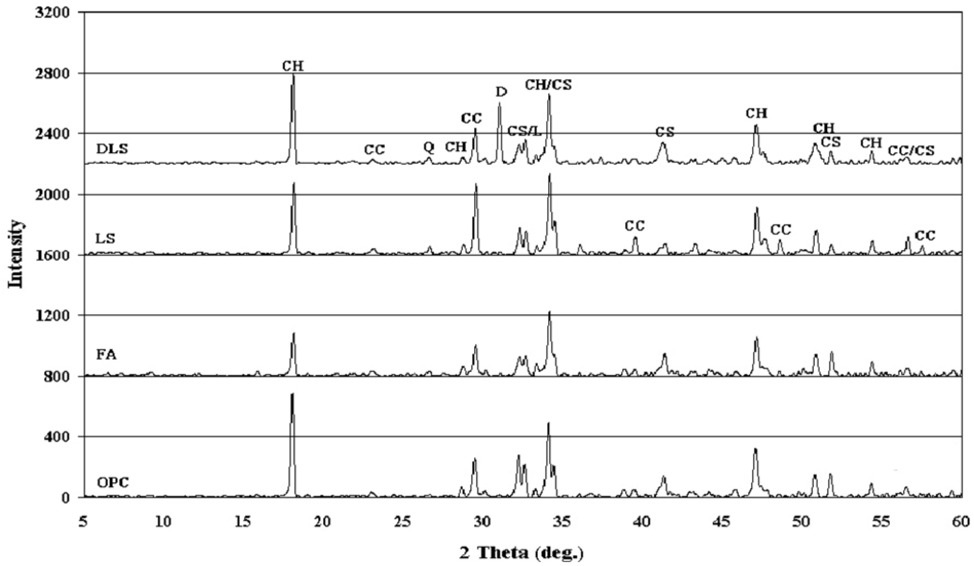

Fig. 4. XRD pattern of the Portland cement and composite cement cured for 2 days. CH, calcium hydroxide; CC, calcium carbonate; CS, tricalcium silicate; L, larnite, D, dolomite; Q, quartz.

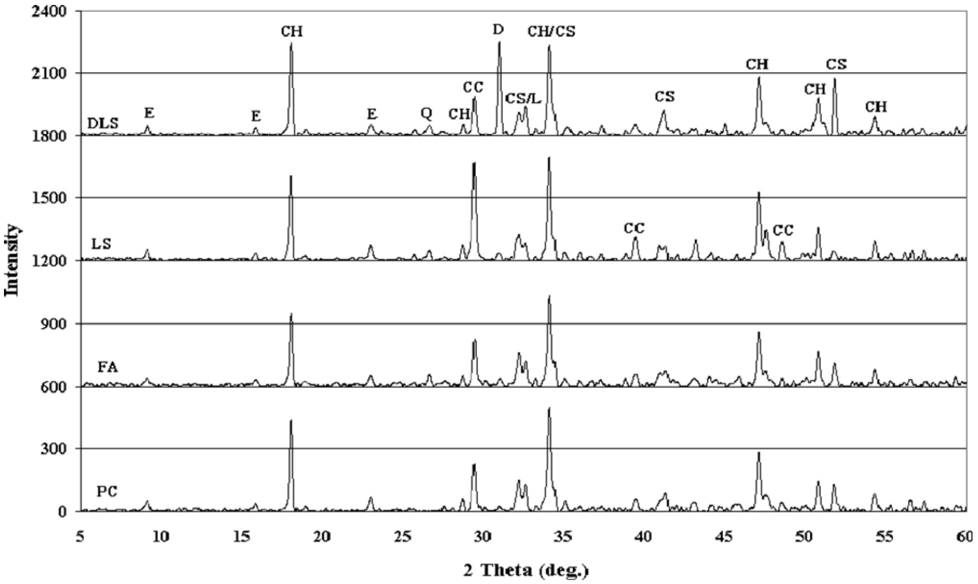

Fig. 5. XRD pattern of the Portland cement and composite cement cured for 7 days. CH, calcium hydroxide; CC, calcium carbonate; CS, tricalcium silicate; L, larnite, D, dolomite; Q, quartz.

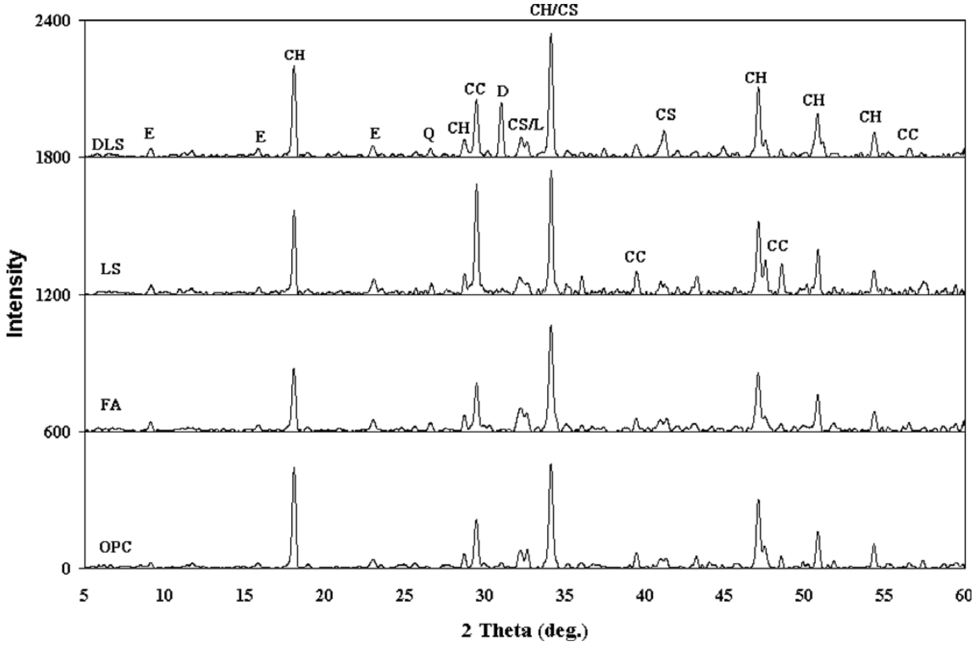

Fig. 6. XRD pattern of the Portland cement and composite cement cured for 28 days. CH, calcium hydroxide; CC, calcium carbonate; CS, tricalcium silicate; L, larnite, D, dolomite; Q, quartz.

X-ray patterns obtained after 2, 7, and 28 days. As it is known, the principal hydration products in composite cement are essentially similar to those found in pure Portland cement. Fig. 4 presents the XRD patterns of the control cement (100% OPC) and composite cement after 2 days of hydration. Calcium hydroxide was formed in appreciable amounts in all samples. However, in composite cement pastes, $Ca(OH)_2$ content was formed in smaller amounts than in control system and the amount present slightly increased with the inclusion of DLS and LS in the cement matrix. All the cements contain $CaCO_3$,with especially strong peak evident in the LS containing cement. The amount of $CaCO_3$ present in the system may be attributed to the unreacted LS and the secondary reactions of $Ca(OH)_2$ and C–S–H with atmospheric CO_2.

Fig. 5 presents the X-ray traces of the samples after 7 days of hydration. Three major crystalline phases identified were portlandite, calcium carbonate, some unreacted di- and tricalcium silicate. Enttringite (AFt) has been formed in all samples. Despite the gradual decrease of clinker content in

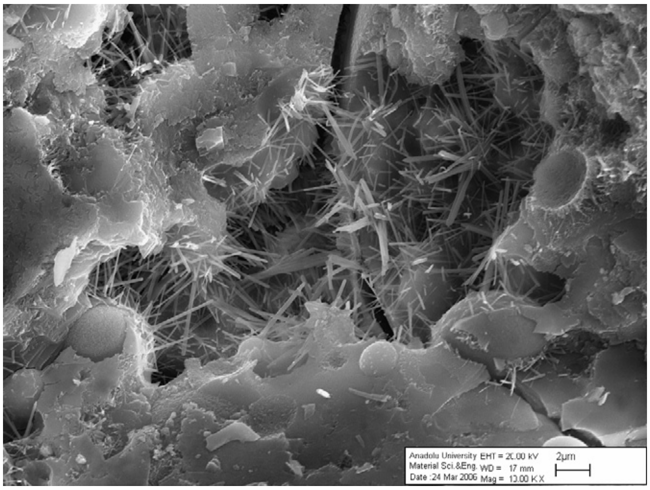

Fig. 7. SEM images of fracture surface of cement paste after 14 days of hydration (the cement used contains 5 G + 10% FA + 10% DLS + 75% PC).

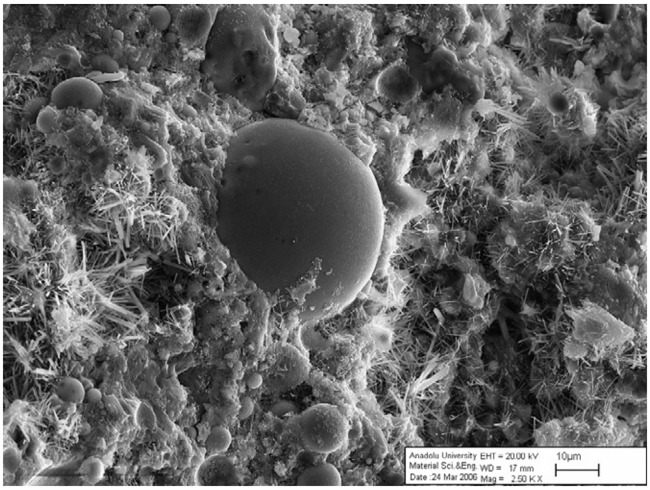

Fig. 8. SEM images of fracture surface of mortar after 14 days of hydration (the cement used contains 5 G + 10% FA + 10% LS + 75% PC).

composite cements, there was no noticeable change in the amount of ettringite formed. As curing time expanded to 28 day (Fig. 6), the amount of $Ca(OH)_2$, unhydrated di- and tricalcium silicate decreased as expected. The amount of calcium carbonate present increased slightly in DLS cement paste. This may be attributed to the reaction between dolomite and calcium hydroxide that result in the formation of calcium carbonate [7].

3.4. Scanning electron microscopy

Figs. 7 and 8 show some microstructural characteristics of the LS and DLS cement pastes cured for 14 days. As can be observed in these figures, the samples studied through SEM/EDX have quite different microstructures. In LS–cement paste, significant quantity of ettringite (AFt phase), $Ca(OH)_2$ (CH) crystals and a porous composite mass of calcium silicate hydrate are observed. Additionally, large amounts of the spherical shape of FA are seen everywhere. In the DLS–cement paste, a very dense structure of CSH has been formed. Due to covering of the FA particles by the reaction products only a small number of round FA particles are distinguished. A significant quantity of ettringite is also evident in DLS–cement paste.

3.5. FT-IR analyses of hydrated cement

The FTIR spectra of the OPC and composite cement hydrated up to 28 days are presented in Figs. 9–11. The major changes of the FTIR spectra in the hydrated cement pastes are:

- The strongest Si–O stretching band (ν_3) appears at $\approx$961 cm^{-1}, and a weak one Si–O bending (ν_5) at about 457 cm^{-1} in all samples. However, the intensity of the Si–O stretching band (ν_3) is lower than that of the composite cement at 2 days curing ages. The relative intensity of the Si–O bending vibrations also undergoes significant changes as curing time is expanded.

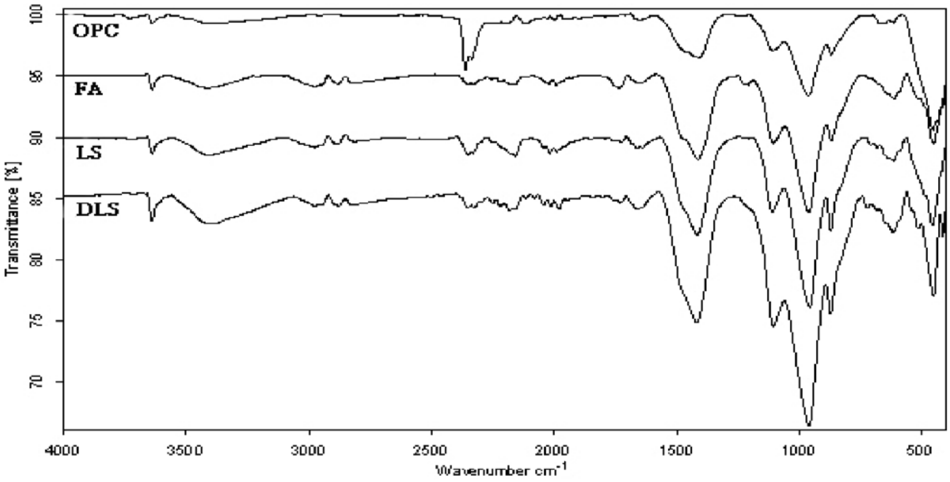

Fig. 9. FTIR spectra of OPC and composite cement cured for 2 days.

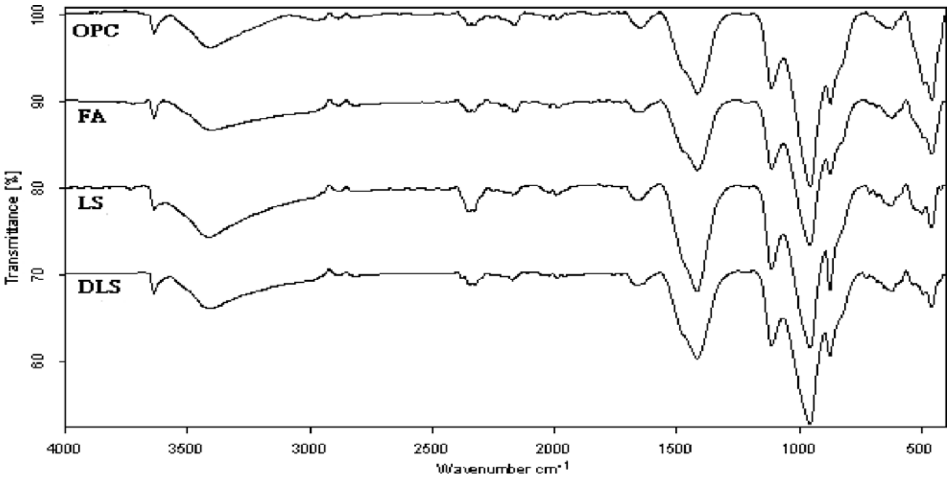

Fig. 10. FTIR spectra of OPC and composite cement cured for 7 days.

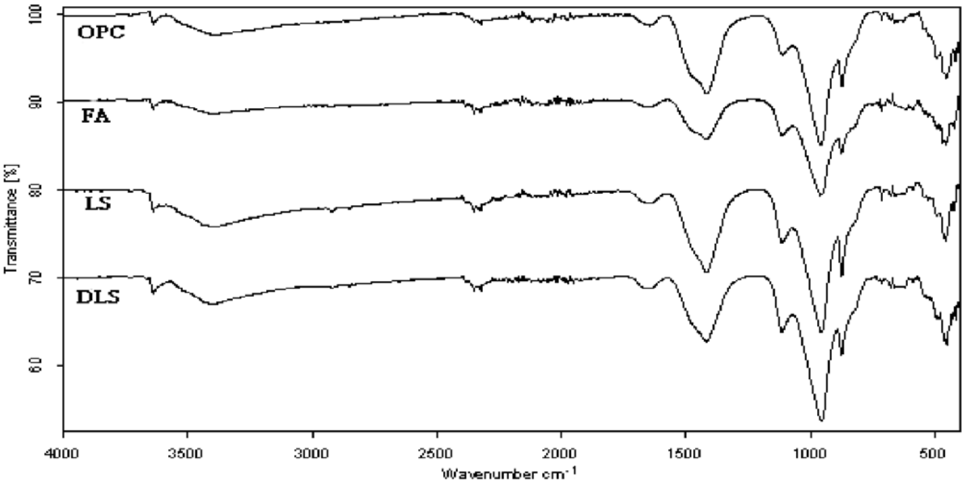

Fig. 11. FTIR spectra of OPC and composite cement cured for 28 days.

- The C–O bending vibration (ν_2) at about 872 cm^{-1} and the C–O stretching (ν_3) at around 1417 cm^{-1} are the characteristic band of CO_3^{2-}.
- The bands at 617–623 cm^{-1} are assigned ettringite, in agreement with XRD analysis.
- The bands appeared at around 1106–1116 cm^{-1} can be assigned to the stretching vibration (ν_3) of gypsum (SO_4^{2-}).
- A broad band centered at ≈3400 cm^{-1} is due to symmetric and antisymmetric stretching vibration of water bound in the hydrations products.
- A small but defined peak appeared at 3637–3641 cm^{-1} can be attributed to the OH band from calcium hydroxide. The intensity of corresponding peak, in the samples containing FA is lower than that of the other tested sample.

4. Conclusions

The following conclusion can be drawn from the obtained experimental data:

1. The hydration products formed in the four systems studied were as expected, although they differed in magnitude. Calcium hydroxide was formed initially in all systems, but the amount of calcium hydroxide formed in the OPC + FA cement paste was less than that formed in the OPC + FA + LS and OPC + FA + DLS system.
2. The compressive strength of the mortar gradually decreases with the increasing fly ash content. However, incorporation of FA with LS and DLS resulted in an increase in the strength of the mortar in comparison with the FA mortar.
3. The setting time and soundness of the FA, LS, and DLS cements are satisfactory and similar to those observed in Portland cement.
4. When combined in ternary system OPC–FA–DLS mortar, the expansion of mortar prism decreases as the dolomitic limestone content increases.

This study has shown that the low-calcium fly ash can be used in the limestone cement and dolomitic limestone cement matrix to control the volume expansion.

References

[1] Duchesne J, Berube MA. Effect of supplementary cementing materials on the composition of cement hydration products. Adv Cem Based Mater 1995;2:43–52.

[2] Lam L, Wong YL, Poon CS. Degree of hydration and gel/space ratio of high-volume fly ash/cement systems. Cement Concrete Res 2000;30:747–56.

[3] Shehata Medhat H, Thomas DA Michail. The effect of fly ash composition on the expansion of concrete due to alkali–silica reaction. Cement Concrete Res 2000;30:1063–72.

[4] Lee CY, Lee HK, Lee KM. Strength and microstructural characteristics of chemically activated fly ash–cement systems. Cement Concrete Res 2003;33:425–31.

[5] Voglis N, Kakali G, Chaniotakis E, Tsivilis S. Portland–limestone cement, their properties and hydration compared to those of other composite cement. Cement Concrete Compos 2005;27:191–6.

[6] Bleszynski RF, Thomas MDA. Microstructural studies of alkali–silica reaction in fly ash concrete immersed in alkaline solutions. Adv Cement Based Mater 1998;7:66–78.

[7] Gali S, Ayora C, Alfonso P, Tauler E, Labrador M. Kinetics of dolomite–portlandite reaction, application to portland cement concrete. Cement Concrete Res 2001;31:933–9.

[8] TS EN-196-1, TS EN-196-3, TS EN-196-6, TS-EN 197-1, Turkish National Standards, TSE Turkish Standard Institute, Ankara, Turkey.

[9] Cyr Martin, Lawrence Philipe, Ringot Erick. Efficiency of mineral admixtures in mortars: quantification of the physical and chemical effects of fine admixtures in relation with compressive strength. Cement Concrete Res 2006;36:264–77.

[10] Matschei T, Lothenbach B, Glasser FP. The role of calcium carbonate in cement hydration. Cement Concrete Res 2007;37:559–64.

[11] Bentz DP. Modelling the influence of limestone filler on cement hydration using CEMHYD3D. Cement Concrete Compos 2006;28:124–9.

[12] Kula I, Olgun A, Erdogan Y, Sevinç V. Effects of colemanite waste, coal bottom ash, and fly ash on the properties of cement. Cement Conrete Res 2001;31:491–4.

[13] Tsivilis S, Chaniotakis E, Badogiannis E, Pahoulas G, Ilias A. A study on the parameters affecting the properties of Portland limestone cement. Cement Concrete Compos 1999;2:107–16.

[14] Zheng L, Xuehua C, Mingshu T. Hydration and setting time of MgO-type expansive cement. Cement Concrete Res 1992;22:1–5.