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Farklı Hacimlerdeki Uçucu Külün Isı İle Kürlenen Hava Sürükleyici Katkılı Çimento Harçlarına Etkisi

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Anahtar Kelimeler
Hava sürükleyici katkı,
Uçucu kül,
Isı kürü,
Mekanik özellikler

Öz: Uçucu külün doğası karbon kalıntısı içermektedir ve yüzey aktif maddeler ile karbon kalıntısı arasındaki etkileşim çimento esaslı malzemelerin performansı için sorun teşkil etmektedir. Buna ek olarak, beton gibi malzemelerin ısı ile kür edilmesi bu tip mikro yapısal bozulmayı daha açık hale getirebilir. Bu konuyu daha fazla detaylandırmak üzere, hava sürükleyici katkı maddesinin, farklı hacimlerde uçucu kül içeren ısı kürü ile kür edilmiş çimento harçları üzerindeki etkisi deneysel bir çalışma ile incelenmiştir. Uçucu kül içeren hava sürükleyici katkılı çimento harçlarının mekanik özellikleri farklı yaşlarda değerlendirilmiştir. Karşılaştırmalı araştırma ayrıca mikro yapısal analizlerle de gerçekleştirilmiştir. Karbon esaslı malzemelerin ve hava sürükleyici katkı maddesinin etkileşimi mekanik ve mikro yapısal bulgular dikkate alınarak ayrıntılı olarak tartışılmıştır. Sonuçlar, hava sürükleyici katkı maddesi ile toplam bağlayıcı malzeme ağırlığınca %25 uçucu kül kullanılmasının, hava sürükleyici katkı içermeyen ısı ile kür edilmiş çimento harçlarına kıyasla olumlu olduğunu göstermektedir. Ancak ısı ile kür edilmiş ve hava sürükleyici katkı maddesi içeren çimento esaslı harçlarda uçucu külün %55'ten fazla kullanımı ise tavsiye edilmemektedir.

Effect of Different Volumes of Fly Ash on Strength and Microstructural Properties of the Air-entrained Cement Mortars Produced with Heat Curing

Keywords
Air-entraining admixture,
Fly ash,
Heat curing,
Mechanical properties

Abstract: The nature of fly ash comprises residual carbon and the tendency of interaction between surfactants and carbon residue poses a problem for the performance of cement-based materials. Moreover, heat curing of concrete-like materials may be more prone to such microstructural degradation. To elaborate further on this issue, an experimental study was carried out to evaluate the effect of air-entraining admixture on the different volumes of fly ash-bearing heat-cured cement mortars. The mechanical properties of air-entrained cement mortars incorporating fly ash were evaluated at different ages. A comparative investigation was also performed with microstructural analysis. The interaction of carbonaceous materials and the air-entraining admixture was further discussed by taking account of the mechanical and microstructural findings. Results indicate that using air-entraining admixture with 25% fly ash by weight of total cementitious materials exhibited promising results in comparison with the heat-cured cement mortars that do not include air-entraining admixture. However, beyond 55% of fly ash by weight of total cementitious materials is not recommended for the air-entrained cement mortars produced with heat curing.

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1. Introduction

The utilization of fly ash to produce more sustainable concrete is a well-documented practice. The appropriate use of fly ash in concrete mixtures results in limited heat of hydration, higher ultimate strength and reduced permeability of microstructure [1-3]. Moreover, fly ash enables to provide mitigation for durability problems such as sulfate attack [4], alkali-silica reactions [5], ingress of deleterious materials [6]. The use of fly ash in high-performance concrete was tested extensively and reported that fly ash incorporated concrete is more resistant to aggressive environments compared to that of fly ash-free concrete matrices [7]. On the other hand, chemical air-entraining admixtures (AEAs) based on surfactant chemistry are used to entrain the homogeneous air-void system in fresh concrete. These chemical admixtures are proved to be very effective in the use of the concrete mixture which exposes to frost action although air void distribution is also affected by other factors. However, it is reported that one of the most significant issues required to be taken into consideration when using fly ash is the adverse effect of air-entrained admixture. [8-10]. The reason for incompatibility is generally attributed to the non-ignited nature of carbon in fly ash [11]. The adsorption of surfactant in air-entraining admixture (AEA) onto carbonaceous material available in the fly ash is the main problem for the combined use of AEA and fly ash in concrete mixtures. [12]. The lack of effectiveness of AEA due to incompatibleness of surfactant and carbonaceous material was reported in the literature for fly ash containing concrete [13]. Accordingly, reduced advantage of AEA lead to concrete mixtures to be more prone to frost actions. To precisely investigate the role of interaction between fly ash and air-entraining admixture, a comprehensive study was carried out on the various replacement ratios of fly ash together with AEA in cement-based composites.

The different types of curing for concrete production may also play significant role in terms of the air-entrained concrete incorporating fly ash. The influence of elevated curing temperature on the properties of cement mortars has been the subject of several studies [16]. The microstructural characteristics of concrete such as C-S-H gels, porosity and the hydration development are known to be affected in heat curing due to the formation of macroporous, nonuniform distribution of hydration products and delayed ettringite formation [17-19]. However, the effect of heat curing is not understood thoroughly on air-entrained concrete incorporating different volumes of fly ash and not encountered in the literature within the knowledge of authors. This study was aimed to clarify the effect of air-entraining on the heat cured cement mortar incorporated different volumes of fly ash. To do this, various mixtures were developed and interaction between AEA and fly ash was investigated in terms of mechanical behavior. In addition, petrographical and thermogravimetric analysis (TGA) were performed as a microstructural investigation to characterize chemical compounds of specimens. Together with microstructural analysis, mechanical findings were further discussed at different ages in accordance with the former experimental results.

2. Material and Method

2.1 Materials

Mixture design for cement mortars includes CEM I 42.5R ordinary Portland cement (PC), Class-F fly ash (FA) and fine silica sand with maximum aggregate size of 2 mm, water absorption capacity of 0.3% and specific gravity of 2.60. Tap water and air-entraining concrete admixture were used in the mixtures according to relevant standard TS EN 934-2 [20]. Chemical/physical properties of dry raw materials are given in Table 1.

Table 1. Chemical composition and physical properties of PC, FA and silica sand

Chemical Composition, %	PC	FA	Silica sand
SiO_2	18.87	61.81	99.79
Al_2O_3	5.62	19.54	0.06
Fe_2O_3	2.54	7.01	0.02
MgO	2.63	1.71	0.01
CaO	62.78	1.77	0.02
Na_2O	0.40	1.50	0.02
K_2O	0.90	1.95	0.01
Loss on Ignition	2.20	2.50	0.07
SiO_2+Al_2O_3+Fe_2O_3	27.03	88.36	99.87
Physical Properties			
Special Gravity	3.06	2.10	2.60
Blaine Fineness (m^2/kg)	325	269	-

2.2. Proportioning and preparation of specimens

Fly ash to Portland cement ratios (FA/PC) were 25/75%, 35/65%, 45/55%, 55/45%, 65/35%, 75/25% by weight, respectively (Table 2). The air-entraining admixture was added at 2% by volume of the total mixture. Water to cementitious materials (W/CM) was kept constant at 0.4 ratios. The same mixtures were also produced without using AEA to compare the results.

Table 2. Proportions of specimens

Mix ID	PC	W/CM	CM/Sand	AEA*	FA/PC**
Mortar25-AEA	1	0.40	0.33	2	0.33
Mortar35_AEA	1	0.40	0.33	2	0.54
Mortar45_AEA	1	0.40	0.33	2	0.82
Mortar55_AEA	1	0.40	0.33	2	1.22
Mortar65_AEA	1	0.40	0.33	2	1.86
Mortar75_AEA	1	0.40	0.33	2	3.00
Mortar25	1	0.40	0.33	-	0.33
Mortar35	1	0.40	0.33	-	0.54
Mortar45	1	0.40	0.33	-	0.82
Mortar55	1	0.40	0.33	-	1.22
Mortar65	1	0.40	0.33	-	1.86
Mortar75	1	0.40	0.33	-	3.00

***** by volume of total mixture; ****** by weight of binder

During the preparation of specimens, tap water was put into a mortar mixer together with the cement and mixing started for 30 seconds in 62 rounds per minute (rpm). Then, silica sand was gradually added into the mixer in 30 seconds and mixing was made for another 90 seconds at 125 rpm. AEA was gradually added into mixer tank for 30 seconds for the relevant mixtures. Similar consistency (flow diameter 20±1) for each AEA incorporated mixture was achieved. Produced mixtures were molded to prismatic specimens with the dimension of 160×40×40 mm. Three specimens were fabricated for each type of mixture at pre-determined test age. Molded fresh mortars were put into heat curing for the first 24 hours at 75 ˚C. After 24 hours, mortars were taken from molds and kept in thermostat controlled curing tank for 27 days in a lime-saturated water at 20±2 ˚C.

2.3. Testing

2.3.1 Mechanical tests

The flexural and compressive strengths of each mixture were evaluated in accordance with standard TS-EN 1015-11, 2000 [21]. The flexural strength of mortars was determined by three-point loading of a 160 x 40 x 40 mm prism specimen. Loading rate was applied at 50 N/s and specimens were placed on supports by 30 mm distance from the two edges of the mortar (Figure 1-a). Compressive strength was determined on each half of 160 x 40 x 40 mm prism specimen by uniaxial loading at 2400 N/s (Figure 1-b). Both tests were conducted at 3, 7, 28 and 90 days by using three specimens for each mixture.

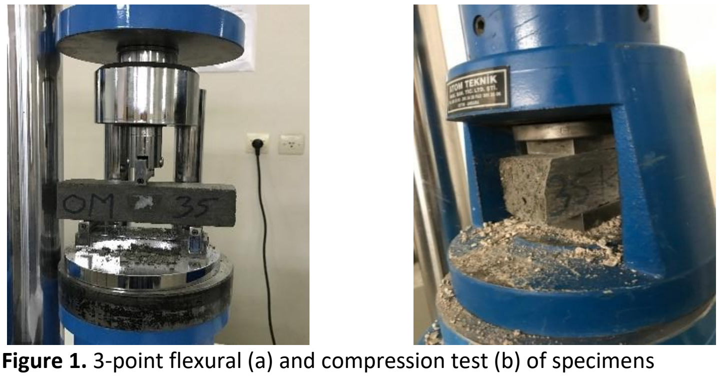

Figure 1. 3-point flexural (a) and compression test (b) of specimens

2.3.2 Microstructural characterization

In addition to the evaluation of mechanical behavior of air-entrained cement mortar incorporating different volumes of fly ash, petrographical analysis was conducted to investigate compounds. Extracted thin samples from each specimen were prepared (Figure 3) and analyzed through polarized microscopes and petrographic analysis with the method proposed by Baccelle and Bosellini (1965) [22]. The components of each mixture were observed and identified.

Figure 2. Thin sections extracted from specimens for petrographical analysis

Besides mechanical tests, microstructural analysis was also performed to qualitatively investigate the microstructural conditions for specimens. To do this, thermogravimetric analyzer (TGA/DTA by Mettler Toledo) having alumina crucible under nitrogen atmosphere was used to have a better insight into the behavior of fly ash- and AEA-bearing specimens. In cement mortars, this technique is particularly useful to measure the consumption of calcium hydroxide by supplementary cementitious materials (SCM) such as fly ash [23]. Accordingly, 50 mg of powdered samples were heated in a flushed air atmosphere at a heating rate of 20 ºC/minute between 25 to 900 ºC in conformity with the relevant standard (ISO 11358). TGA measurements were calculated in accordance with the evaporation and decomposition of specimen products while DTG measurements were conducted to evaluate the temperature regions for the significant mass loss recorded for the specific compounds of the mixtures.

3. Results and Discussion

3.1 Mechanical tests

3.1.1 Compressive strength

The compressive strength of cement mortars was evaluated at 3, 7, 28 and 90 days. Test results were presented in Table 3 and Figure 4.a-f. Heat curing clearly accelerated the compressive strength of cement mortars at early ages without regard to the presence of AEA in mixtures. The early age strength gain by the utilization of heat curing is due to the high temperature that accelerated the cement hydration [24].

Table 3. Compressive strength of cement mortars at 3, 7, 28 and 90 days

Mix ID	3 days	7 days	28 days	90 days
Mortar25_AEA	20.71	25.44	31.34	40.80
Mortar35_AEA	17.48	21.64	29.08	35.56
Mortar45_AEA	15.49	17.19	26.16	30.50
Mortar55_AEA	13.19	14.64	20.34	25.82
Mortar65_AEA	7.99	9.01	16.47	23.64
Mortar75_AEA	6.26	8.82	12.00	13.46
Mortar25	18.39	24.47	31.83	43.76
Mortar35	17.90	22.00	31.43	36.09
Mortar45	17.26	18.33	26.76	33.75
Mortar55	13.31	14.81	20.78	26.13
Mortar65	11.66	12.07	17.61	24.43
Mortar75	9.29	9.50	12.84	15.64

At 3 days, the compressive strength of all AEA-bearing mortars was lower than reference specimens except Mortar25_AEA mixture (Figure 4.a). The compressive strength of Mortar25_AEA was 12.6% higher than its counterpart that does not contain AEA at 3 days. Mortar35_AEA, Mortar45_AEA, Mortar55_AEA, Mortar65_AEA, Mortar75_AEA specimens exhibited 2.3%, 10.2%, 1%, 31.5% and 32.6% lower compressive strength than Mortar35, Mortar45, Mortar55, Mortar65, Mortar75 specimens, respectively. As can be understood in Table 3, a lesser early compressive strength of air-entrained mortars incorporated fly ash can be considered negligible especially for Mortar35_AEA, Mortar45_AEA, Mortar55_AEA mixtures. Generally speaking, 1% of AEA incorporation may reduce the compressive strength of ordinary Portland cement concrete up to 10% as Mehta et al. (2006) suggested [25]. For this reason, a decrease of 10% of compressive strength can be expected to take into account the fact that 2% of AEA used in the present study. This reduction can also be mitigated easily by some adjustments in mixture proportioning. However, 65% and 75% fly ash incorporated specimens by weight of total cementitious materials resulted in a distinct reduction in compressive strength at 3 days. This can be attributable to the higher pozzolanic materials available in the mortar matrices which could not have reacted with calcium hydroxide (CH) yet at 3 days. Also, as higher fly ash content corresponds to higher carbon available in the system, the higher probability of absorption of AEA bubbles onto fly ash particles may have led to weak zone and may have created undistributed air bubbles in the cement mortars. This may have reduced the cross-section area of mortars resisting under compression loading. The only mixture that acted adversely on this behavior was Mortar25_AEA, as previously mentioned. The reason can be explained by the lesser fly ash content that means a lower chance of carbonaceous exposure for AEA. Accordingly, air-entraining bubbles could have been distributed much more homogeneously. This finding is in line with the latest study performed by Puthipad et al. 2018. The amount of coalescence of air-entraining bubbles increases when the fly ash is used at higher ratios irrespective of AEA type [26]. Moreover, although air-entraining bubbles are expected to decrease the compressive strength of Mortar25_AEA specimens, the results were not in this line. Absorption of AEA was probably remained limited and more homogeneously distributed air-entraining bubbles were formed in Mortar25_AEA mixture. Also, spherical shape of AEA bubbles may have provided a lubricating effect on the fresh properties of AEA-bearing mortars [25] so that better workability properties may have created lesser weak zones [27]. This could have offset the detrimental voids of Mortar25_AEA mixture for compressive strength. 12.6% increase of average compressive strength of mortar25_AEA can be also explained by the improved particle distribution of the cementitious system by forming dense microstructure. On the other hand, in the case of fly ash increment, the compressive strength of mortars decreased at 3 days irrespective of AEA presence, as expected [28]. This trend is understandable since cementing ability of fly ash contributes only after hydration takes place between water and cement. So, a lesser amount of available CH can be available to react with fly ash particles to form hydration products at 3 days.

At 7 days, the similar trend can be also observable for the compressive strength of cement mortars. The compressive strength of Mortar25_AEA was 4% higher than reference mortar that does not contain AEA at 7 days (Figure 4.a). Mortar35_AEA, Mortar45_AEA, Mortar55_AEA, Mortar65_AEA, Mortar75_AEA specimens exhibited 1.6%, 6.2%, 1.1%, 25.3% and 7.1% lower compressive strength than Mortar35, Mortar45, Mortar55, Mortar65, Mortar75 specimens, respectively (Figure 4.b-f). 25% fly ash incorporated cement mortars by weight of binder (Mortar25_AEA) did not exhibit as higher compressive strength (4%) as the same mixture exhibited at 3 days (12.6%) compared to control mix. This can be related to the increased cementing capability of fly ash at 7 days as the mixtures started to saturate. Also, reductions of compressive strength were recorded for the 65% and 75% fly ash incorporated specimens by weight of total cementitious materials (25.4% and 7.2%, respectively) at 7 days, as given in Figure 4. Similarly at 3 days of curing, the increased fly ash content also resulted in lower compressive strength without regard to AEA addition at 7 days.

The behavior of cement mortars under compressive loadings changed at 28 days, as can be followed in Table 3 and Figure 4. Unlike test results at 3 and 7 days, compressive strength of 28 day-old Mortar25_AEA was 1.5% lower than the compressive strength of Mortar25. Also, Mortar35_AEA, Mortar45_AEA, Mortar55_AEA, Mortar65_AEA, Mortar75_AEA specimens exhibited 7.5%, 2.2%, 2.1%, 6.5% and 6.5% lower compressive strength than Mortar35, Mortar45, Mortar55, Mortar65, Mortar75 specimens, respectively. The reductions of compressive strength were comparable for all mixtures at 28 days. However, compressive strength of cement mortars was slightly lower than the similar cement mortars studied without heat curing in the literature. Therefore, the reductions in compressive strength were more influential in air-entrained cement mortars at later ages (at 28 days). This can be attributed to the reduced cross-section area of mortars due to entrained air bubbles and detrimental effect of heat curing on the account of larger hydration products formed at early ages which are unable to fill smaller voids.

The results of compressive strength at 90 days are in similar trend with the results at 28 days (Figure 4). For example, Mortar25_AEA, Mortar35_AEA, Mortar45_AEA, Mortar55_AEA, Mortar65_AEA and Mortar75_AEA specimens exhibited 6.7% 1.5%, 9.6%, 11.8%, 3.2% and 14% lower compressive strength than Mortar25, Mortar35, Mortar45, Mortar55, Mortar65 and Mortar75 specimens, respectively. As can be seen from the results, the highest reduction of compressive strength was recorded for Mortar75_AEA specimens at 90 days (%14). It is probable that incorporation of 2% of AEA by volume of mixture together with the high content of fly ash (75%) might have created additional weak zones due to the adsorption of AEA surfactant onto residual carbon content (2.5% [Table 1]) of fly ash.

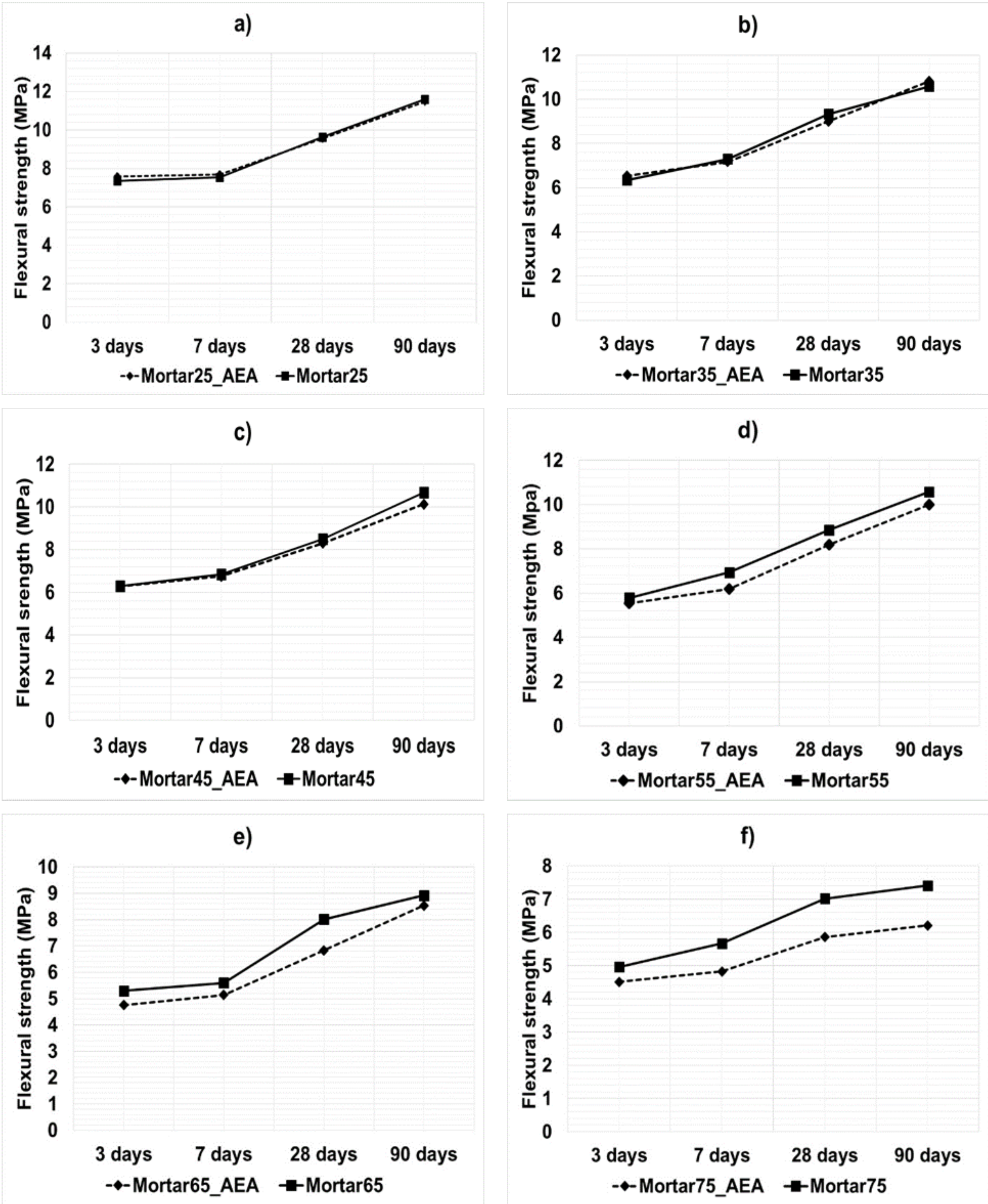

Figure 3. Comparison of compressive strength between air-entrained cement mortars and reference cement mortars with regard to fly ash content a) 25% b) 35% c) 45% d) 55% e) 65% f) 75% by weight of total binder at 3, 7, 28 and 90 days

3.1.2 Flexural strength

The flexural strength of cement mortars was evaluated at 3, 7, 28 and 90 days. Tests results were given in Table 4 and Figure 5.a-f.

Table 4. Flexural strength of cement mortars at 3, 7, 28 and 90 days

Mix ID	3 days	7 days	28 days	90 days
Mortar25_AEA	7.59	7.70	9.56	11.49
Mortar35_AEA	6.54	7.17	9.00	10.83
Mortar45_AEA	6.28	6.76	8.30	10.14
Mortar55_AEA	5.55	6.19	8.19	10.01
Mortar65_AEA	4.76	5.14	6.84	8.54
Mortar75_AEA	4.51	4.83	5.86	6.21
Mortar25	7.36	7.54	9.63	11.60
Mortar35	6.34	7.30	9.33	10.59
Mortar45	6.29	6.84	8.50	10.67
Mortar55	5.79	6.94	8.86	10.58
Mortar65	5.30	5.60	8.02	8.92
Mortar75	4.96	5.67	7.02	7.41

High-temperature curing (heat curing at 75 ^{o}C) clearly exhibited higher flexural strength than cement mortars cured in normal conditions at 3 and 7 days due to activation energy, as expected and also reported by literature studies [29]. This finding supports that heat curing conducted for 24 hours at 75 oC accelerated the hydration process. Accordingly, early age flexural strength of cement mortars increased without regard to air-entraining admixture. At 3 days, the flexural strength of all air-entrained cement mixtures was lower than reference specimens except Mortar25_AEA and Mortar35_AEA mixtures (Figure 4.a-b). The flexural strengths of Mortar25_AEA and Mortar35_AEA were 3.1% and 3.2% higher than Mortar25 and Mortar35 mixtures, respectively. This slight increase of flexural strength is probably due to optimum increased activation energy thanks to curing at high temperature for the given fly ash content [29]mitigating the negative effect of AEA for flexural strength. It can be said that use of 25% fly ash by weight of total binder can be regarded as optimum threshold taking into account compressive and flexural strength results in the presence of 2%-AEA. The higher fly ash content resulted in a reduction of flexural strength for the air-entrained cement mortars compared to their reference mixtures. For example, the flexural strength of Mortar55_AEA, Mortar65_AEA, Mortar75_AEA specimens were 4.1%, 10.1%, and 9% lower than Mortar55, Mortar65, Mortar75 specimens at 3 days, respectively. Similar behavior can be also followed at 7 days for the air-entrained cement mortars incorporated fly ash. Except for Mortar25_AEA mixture, other mixtures exhibited lower flexural strength than mortars without air-entraining. At 7 days, higher reduction of flexural strength of Mortar 65_AEA and Mortar75_AEA (8% and 15%, respectively) can be explained by the higher chance of carbonaceous contact with AEA resulting in non-uniform void distribution.

The air-entrained cement mortars totally underperformed in terms of flexural strength at 28 and 90 days in comparison with the plain cement mortars incorporated fly ash. However, comparable results were recorded for Mortar 25_AEA and Mortar35_AEA mixtures. At 28 days, Mortar25_AEA, Mortar35_AEA, Mortar45_AEA, Mortar55_AEA, Mortar65_AEA, Mortar75_AEA specimens were 0.7%, 3.5%, 2.3%, 7.5%, 14.7% and 16.5% lower in flexural strength than Mortar25, Mortar35, Mortar45, Mortar55, Mortar65, Mortar75 specimens, respectively. As seen in Table 4, reduction of flexural strength at 90 days was higher beyond the use of 65% fly ash by weight of the total binder. Reduction of flexural strength of high-volume fly ash incorporated specimens was expected to disappear at later ages, however, this was not the case. This finding suggests that heat-cured air-entrained cement mortars could have been more susceptible to the detrimental effect of the contact between residual carbon and AEA surfactants. Curing with the elevated temperature is reported to have a significant influence on hydration process resulting in an increased proportion of large pores in cement paste [30]. Therefore, additional fly ash ratio into cement mortars could have led to weaker microstructure due to incompatibility of AEA and fly ash under heat-curing.

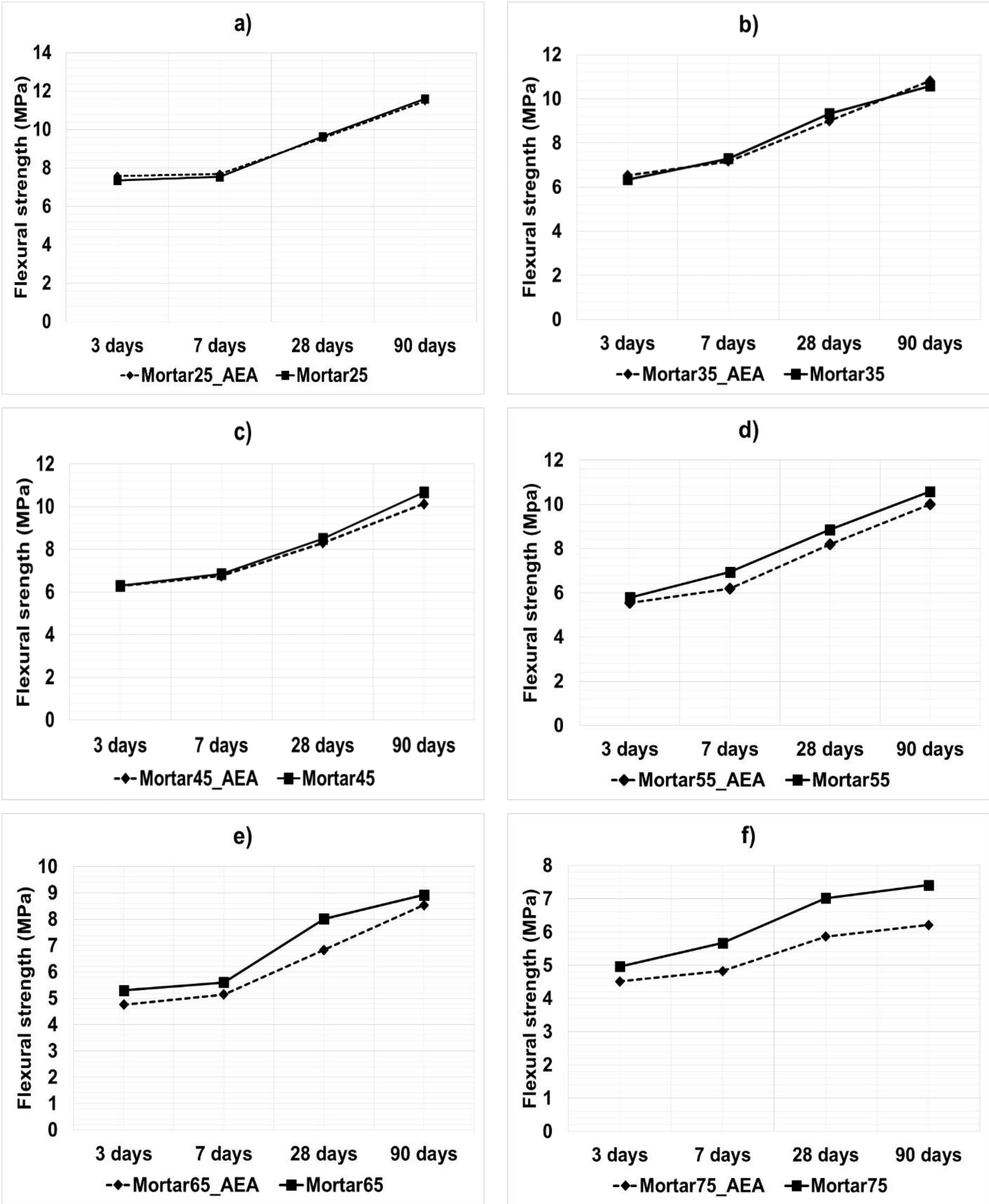

Figure 4. Comparison of flexural strength between air-entrained cement mortars and reference cement mortars with regard to fly ash content a) 25% b) 35% c) 45% d) 55% e) 65% f) 75% by weight of total binder at 3, 7, 28 and 90 days

3.2 Microstructural Tests

3.2.1 Petrographical analysis

Prepared thin sections from each specimen were analyzed petrographically at 28 days. Compounds of each mixture were identified and given in Table 5.

Table 5. Petrographical analysis of specimens at 28 days

Mix ID	Total porosity (%)	Fly ash (%)	Cement paste (%)	Sand<2mm (%)
Mortar25_AEA	10.2	2.8	45	42.0
Mortar35_AEA	10.7	4.4	47	37.9
Mortar45_AEA	12.4	5.0	42	41.6
Mortar55_AEA	12.8	5.2	38	44.0
Mortar65_AEA	13.1	6.7	34	46.2
Mortar75_AEA	13.2	8.3	33	45.5
Mortar25	9.7	3.1	43	44.2
Mortar35	9.7	3.2	42	45.1
Mortar45	9.4	3.8	48	38.8
Mortar55	9.2	4.7	49	37.1
Mortar65	9.2	6.9	52	31.9
Mortar75	9.2	7.5	51	32.3

As can be seen in Table 5, air-entrained cement mortars have higher porosity than the reference mortars without regard to fly ash content, as expected. However, the least porosity difference can be observed between Mortar25_AEA and Mortar25. Moreover, cement paste rate of Mortar25_AEA is 4.4% higher than the Mortar25 specimens due to probable reasons as stated previously. This result supports mechanical findings that 25% of fly ash incorporation into air-entrained cement mortars are comparable with their reference specimens. Similarly, Mortar35_AEA has higher cement paste than Mortar35 mixtures according to the given results in Table 5. However, the total porosity of Mortar35_AEA is higher than the Mortar25_AEA which means a higher chance of the reduction in mechanical properties is possible compared to their reference counterparts at 28 days. An increased porosity rate along with fly ash content implies that air bubbles had more tendency to form near carbonaceous materials resulted in non-uniform voids entrained into the mortar matrices. In Figure 5, microscopic image of mixture incorporated 75% fly ash and 2% AEA (Mortar75_AEA) can be seen.

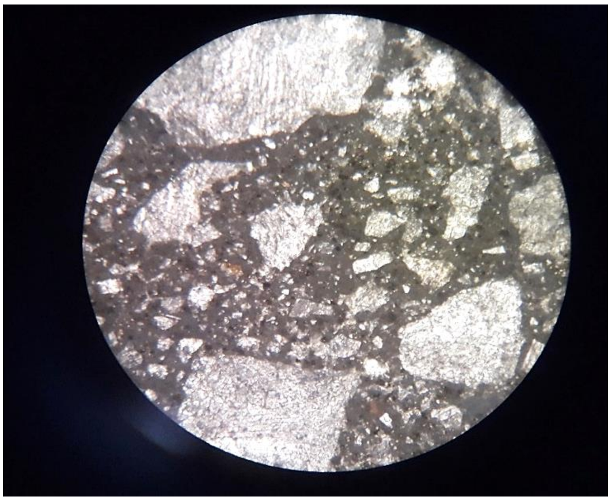

Figure 5. Microstructure of air-entrained cement mortar incorporated 75% fly ash by weight of total cementitious materials (image is within 1000µ diameter)

Also, interaction of residual carbon in LOI and air-entraining admixtures probably affected the rate of cement paste in mortars. This made the mixtures having more weak zones between hydration products thus increasing overall porosity. The findings of petrographical analysis are in line with the results of compressive and flexural strength results. Therefore, it can be suggested that only 25% fly ash content may not have negative effect to the mechanical properties of cement mortars in the presence of 2% AEA by volume of total mixture.

3.2.2 TGA/DTA analysis

The thermogravimetric analysis (TGA) was conducted to evaluate the composition of the fly ash-bearing air-entrained cement mortars. TGA/DTA was used to evaluate the change in mass of a material with the increase in temperature. As given before (Table 1), loss on ignition (LOI) of fly ash is (2.5% based on the standard LOI test) generally regarded as the carbon content of ash. However, this may be inadequate knowledge because weight change of fly ash can be also due to calcination of carbonates, desorption of bound water, and oxidation of other minerals. To elaborate aforesaid findings, a carbon content of mixtures together with other hydration products such as bounded water, C-S-H, calcium hydroxide (CH) and calcite were investigated through TGA/DTA analysis. However, it can be inferred that decomposition of carbonaceous materials in cement mortars was not explicit although the mass change of water, C-S-H, CH and calcite compounds were clearly seen in Figure 6.

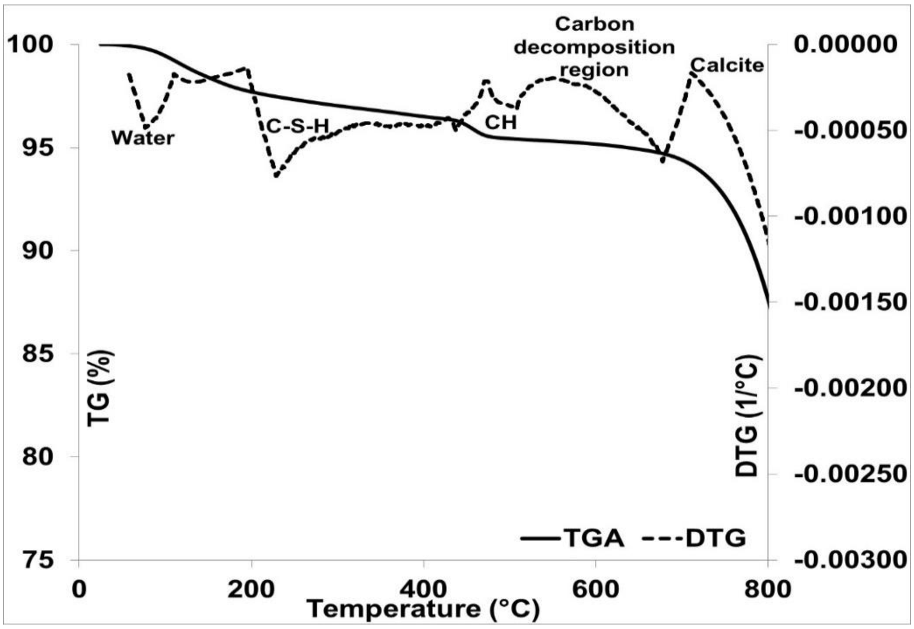

Figure 6. TGA and DTA curves of Mortar25_AEA at 28 days

The results were in line with the studies in the literature [31] that oxidation of carbon-based materials can be seen at different temperatures. However, the mass change of carbon materials may have started between 650-700 C°. According to the suggestion of Paya et al. (1998) [32], carbonaceous materials are oxidized at temperatures between 450°C and 750°C. The smooth slope of TGA-DTA curves of air-entrained cement mortar (Mortar25_AEA) between 450°C and 650°C indicates that decomposition can be only started after 650 C° where sudden drop continues until 750 C° (Figure 6). This temperature gap was also validated by Yu et al., (2000) [33]. Moreover, Fan and Brown (2001) [34] reported that volatile organic compounds (VOCs) in fly ash are decomposed when a specimen is heated to 750 C°. A precise temperature range for the VOCs that are decomposed from fly ash has not been revealed, however, mass change of coal begins at the temperatures between 350 and 400ºC [35]. The presented figure shows that decomposition of carbon compounds could have only started after the temperature of 650 C° because other compounds of cement mortars have characteristically compatible and easily identifiable in accordance with their decomposition temperatures [36]. For example, decompositions of water and C-S-H products were at the temperatures of 90 C° to 170 C°. Also, CH products were vaporized between 430 and 480 C° while calcite compounds were fully decomposed at 770 C°, as seen in Figure 6.

4. Conclusions

This study investigated the interaction between air-entraining admixture and increased fly ash content in heat cured cement mortars. To characterize the mechanical properties, compressive strengths and flexural strengths of air-entrained cement mortars incorporated different amount of fly ash were evaluated. Also, the microstructural investigation was performed through petrographical and TGA/DTA analysis. Mechanical and microstructural characterizations were compared, and the presented study reached the following conclusions:

•Heat curing increased the early age strength of cement mortars both in compressive and flexural strength at 3 and 7 days without regard to the presence of air-entraining admixture. Generally, AEA-bearing cement mortars incorporated fly ash were lower than reference specimens in compressive and flexural strength at all ages.

However, the inclusion of 25% fly ash by weight of total cementitious materials into air-entrained mortar matrices made mechanical results comparable with specimens that do not contain AEA.

•An increased fly ash content in air-entrained cement mortars posed a negative effect on mechanical properties. It can be deduced that detrimental effect of carbonaceous materials in contact with air-entraining bubbles can be offset by limiting the fly ash utilization to a certain extent (25%).

•Petrographical analysis revealed that inhomogeneous distribution of air-entraining bubbles in cement mortars due to increased fly ash content promoted additional porosity by worsening void space. In the petrographical analysis, thin sections of specimens indicated that only 25% fly ash included cement mortars can be excluded from the worsened of void space.

•Similar to the LOI test, TGA/DTA analysis cannot individually evaluate the carbon content of fly ash in mortars. As decomposition of carbonates occurs at the temperatures in which carbonaceous materials oxide, higher amounts of carbonates prevented to the measurement of carbon content in TGA/DTA tests. However, it is probable that the mass change of compounds in LOI content took place between 650-700 C°.

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