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Improvement of Khorasan mortar with fly ash for restoration of historical buildings

Abstract: In this study, the effects of fly ash on Khorasan mortar composed of brick or tile powder and lime were investigated to improve its mechanical properties. In the mixtures, fly ash was used instead of 0- to 4-mm crushed tile or 0- to 1-mm tile powder as aggregate. In addition, slaked lime was used as a binder, and 0–10–20–30–40% fly ash was replaced with crushed tile or tile powder. The consistency, hardened unit weight, ultrasonic pulse velocity, compressive strength and flexural strength before and after exposure to freeze-thaw, and the microstructure and chemical composition of specimens were examined. Scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and thermogravimetric analysis were conducted on specimens. On the basis of the results, notable improvements were observed in the mechanical properties of specimens with addition of fly ash.

Keywords: fly ash; Khorasan mortar; pozzolanic activity; slaked lime; waste tile.

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1 Introduction

Mortars including brick-tile powder and lime have been used in historical buildings since ancient times. Today, the restoration of historical buildings can be achieved by using original materials. Hence, the improvement of ancient mortars used in restoration of historical buildings is important. Mortars containing lime have been used widely by the ancient Greeks, Romans, and Ottomans until the invention of hydraulic cement [1–3]. Khorasan mortar has been used in Ottoman buildings as early as the 15th century [4–6]. In general, such mortars were used by the Romans, Byzantines, Seljuks, and Ottomans in the construction of wells, cisterns, and baths, which have survived up to now [7–9]. Mixing of brick or tile dust and similar materials with mortars containing lime was used in many historical constructions [10–12]. Hence, Turkish, Roman, Byzantine, and medieval mortars and plasters have been studied by several authors [13–15].

During the Ottoman times, lime was mixed with water to form slaked lime and then heated and sifted for use in mortars [16, 17]. Egg whites were mixed with slaked lime and hydraulic brick powder and straw were added to the mixture. The lime reacts with brick or tile dust to produce calcium silicate hydrates (CSHs). The water-absorption capability of porous brick dust allows mortars to gain adhesion and strength in moisture, and the addition of straw particles gives ductility and flexibility during the drying and settling process.

Nonhydraulic mortars including lime are mixed with inactive aggregates [1]. Such mortars are hardened by the reaction of lime and carbon dioxide to form calcium carbonate [1]. Hydraulic mortars are obtained by mixing lime with pozzolans [1]. Crushed brick or tile dust has been used as an aggregate in the production of mortars including lime [3]. Such mortars are called Khorasan in Turkey, Homra in Arabic countries, Surkhi in India, and Cocciopesto in ancient Rome [3]. Khorasan mortar is generally produced by using slaked lime as a binder with various proportions of sand and brick powder as aggregates [2]. Other organic and inorganic materials are sometimes mixed in mortars to improve the quality of the mixture. The mortars produced by mixing crushed bricks using slaked lime and water have adequate mechanical strength [3].

Lime is classified into several groups according to the production process, such as quicklime, hydraulic lime, nonhydraulic lime, and hydrated lime [18]. In general, nonhydraulic lime (lime putty or slaked lime) was used in ancient mortars, whereas hydraulic and hydrated mortars are industrial mortars of the latest century that need specific heating, pulverization, and production methods. All types of lime were produced with water and limestone [18]. However, they differ in the production process, admixture, and water contents.

Brick-lime mortars can be grouped as hydraulic and nonhydraulic due to chemically bound water of hydraulic products [3]. Ancient hydraulic mortars generally consisted of artificial pozzolanic aggregates obtained

from bricks or tiles that were produced by firing at a temperature of 900°C [1]. Clay loses its pozzolanic property over 900°C. However, at present, it is slightly difficult to find industrial bricks or tiles with high pozzolanic activity owing to higher firing temperatures during production. Therefore, waste bricks and tiles obtained from old buildings can be used as pozzolanic aggregate after pulverization. Admixtures can be added to mixtures to obtain adequate mechanical and physical properties in brick-lime mortars. In this study, fly ash (FA) was used as an admixture; on the basis of the results, improvements were observed in mortars with increasing replacement ratios of FA. The aim of the study was to obtain adequate mechanical strength in specimens by using tile powder, crushed tile, lime, and FA despite the low pozzalonic activity of industrial waste tiles.

2 Materials and methods

2.1 Materials

2.1.1 Slaked lime

Slaked lime from Akay Lime Factory (Adana, Turkey) was used in mixtures of Khorosan mortars. The chemical and physical properties of lime used in Khorosan mortar were suitable according to the Turkish Standard, as shown in Table 1 [19]. The bulk density of lime used in experiments was 460 kg/m^3. Calcium hydroxide, traditionally called slaked lime, is an inorganic compound. It is a colorless crystal or white powder and is obtained by mixing calcium oxide with water. Calcium hydroxide is used in many applications including the construction industry.

Table 1 Chemical and physical properties of slaked lime.

Chemical composition	Value (%)
CaO+MgO	92
MgO	1.5
SO_3	0.8
CO_2	4
Insoluble substance+SiO_2	1
R_2O_3	0.5
LoI	0.2
Physical properties	
630 μm (over sieve)	0.5
90 μm (over sieve)	4
Bulk density (kg/m^3)	460

2.1.2 Crushed tile and tile powder

Waste tiles from Kılıcoglu Tile Factory (Eskişehir, Turkey) were used in mixtures of Khorosan mortars. In general, the raw materials of tile and bricks are natural clay with quartz, feldspar, and various minerals [3]. The minerals existing in tile powder were examined by thermogravimetric analysis (TGA) in the study. The tiles were crushed and ground into sizes of 0–1 and 0–4 mm. The crushed tiles were sifted and grouped according to size and labeled as crushed tile (CT) and tile powder (TP). The unit weight and specific gravity of CTs were 1210 kg/m^3 and 2.63, respectively.

2.1.3 Fly ash

FA from Seyitomer Thermal Power Plant (Kütahya, Turkey) was used in mixtures of Khorosan mortars. The chemical and physical properties of FA are shown in Table 2. The total SiO_2, Al_2O_3, and Fe_2O_3 content of FA was >70% and the CaO content was <10%; therefore, the FA of Seyitomer is classified as class F (low lime) with respect to the ASTM standard [20].

2.1.4 Water

Local tap water of Municipality of Eskişehir, Turkey was used in mixtures of Khorosan mortars. The water was found suitable to use as mixing water according to its chemical analysis [21].

2.2 Mixture preparation and proportions

The specimens were produced by replacing either 0-10-20-30-40% CT or TP with FA, and slaked lime was added

Table 2 Chemical and physical properties of FA.

Chemical composition (%)	FA
SiO_2	54.49
Al_2O_3	20.58
Fe_2O_3	9.27
CaO	4.26
MgO	4.48
Na_2O	0.65
K_2O	2.01
SO_3	0.52
Cl	0.002
LoI	3.01
Free lime	0.26
Physical properties	
Specific gravity	2.34
Specific surface (cm^2/g)	4320

as a binder while mixing. The optimum water content was found at the end of several trials. Lime-water ratio was 1:2, and standard molds of sizes 4 cm×4 cm×16 cm were used in mixture production. The slaked lime, FA, either CT or TP, and water were mixed at a low speed. The water was mixed with three equal quantities for each mixture to ensure homogeneity. Subsequently, mixtures of Khorasan mortars were molded and subjected to vibration for 2 s. The mortar specimens were kept for 72 h in the molds and then demolded and subjected to curing for 7 and 28 days at 20±3°C and 50±3% humidity before testing. The mixture and series codes depending on ratios and curing period are shown in Tables 3 and 4, respectively.

2.3 Test methods

The consistency of mortar mixtures was measured by a mortar flow table according to Turkish Standard [22]. The funnel was filled with mortar to obtain the slump flow of each mixture. The flow was found by measuring the mean diameter of a sample.

The unit weights of hardened specimens were measured by sensitive balances; ultrasonic pulse velocities of specimens were calculated by ultrasonic test equipment according to the ASTM standard [23]; flexural strengths were calculated by Michaelis cement testing equipment.

Table 3 Mixture ratio.

Pozzolan	Mix. code	FA	CT	TP	Lime	Water
0–4 mm CT	CTFA0	0.0	2.0	0	1	2
	CTFA10	0.2	1.8	0	1	2
	CTFA20	0.4	1.6	0	1	2
	CTFA30	0.6	1.4	0	1	2
	CTFA40	0.8	1.2	0	1	2
0–1 mm TP	TPFA0	0.0	0	2.0	1	2
	TPFA10	0.2	0	1.8	1	2
	TPFA20	0.4	0	1.6	1	2
	TPFA30	0.6	0	1.4	1	2
	TPFA40	0.8	0	1.2	1	2

Table 4 Series code.

Series code	Cure period
CTFA-0	Fresh
CTFA-7	7 Days
CTFA-28	28 Days
TPFA-0	Fresh
TPFA-7	7 Days
TPFA-28	28 Days

Compressive strengths of specimens were measured by a point load test machine according to Turkish Standard [24]. The compressive strength test was conducted on half of the remaining specimens after flexural strength test. Tests were conducted on specimens on the 7th and 28th days. Additionally, the compressive and flexural strengths of specimens on the 28th day were investigated after freeze-thaw in water according to the ASTM standard [25].

Microstructure and chemical analyses were conducted on the TPFA20 series. The microstructure, morphology, and chemical composition were examined by scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) (Zeiss-Supra 30VP, Jena, Germany) and X-ray diffraction (XRD) (Panalytical-Empyrean, Almelo, Holland), and the hydraulic property of the sample was examined by TGA (Setaram Labsys evo, Lyon, France).

3 Results and discussion

3.1 Consistency of mortar mixtures

The flow diameters of mixtures containing FA were higher compared to that of control specimens. This can be explained by the higher water-absorption capacity of CT and TP compared to FA. The flow diameters increased with increasing replacement ratios of FA as shown in Figure 1. The maximum flow diameter was 18 cm in CTFA40-0.

3.2 Hardened unit weight

The change in hardened unit weight according to FA ratio is shown in Figure 2. The hardened unit weight of specimens cured for 7 days was higher than those of specimens

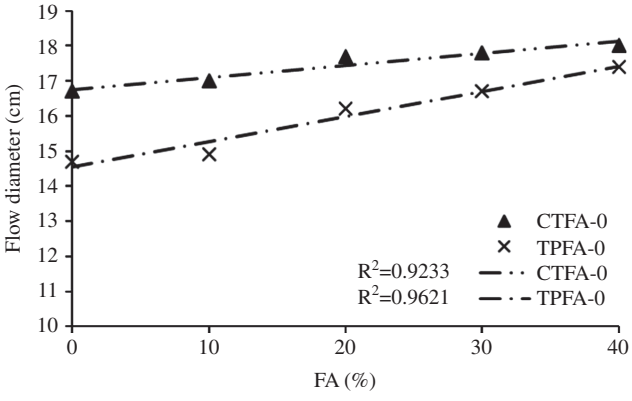


Figure 1 Flow values of fresh mixtures.

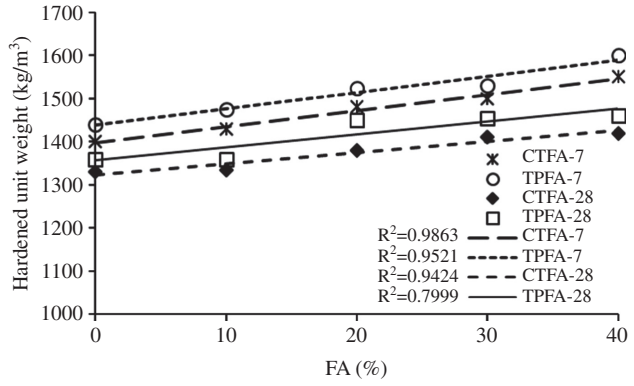


Figure 2 Hardened unit weight of specimens.

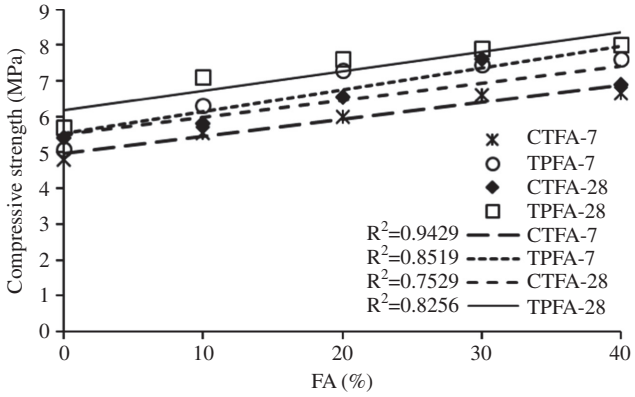


Figure 4 Compressive strength of specimens.

cured for 28 days. This can be explained by the higher water content of specimens at the early ages. The increase in hardened unit weight can be explained by the higher water absorption capacity of CT and TP at the early ages compared to the FA. The hardened unit weight of specimens containing FA was higher than those of control specimens. Furthermore, the TPFA series had higher hardened unit weights compared to the CTFA series. The maximum hardened unit weight was 1600 kg/m^3 in TPFA40-7.

3.3 Ultrasonic pulse velocity

The change in ultrasonic pulse velocity depending on FA ratios is shown in Figure 3. The ultrasonic pulse velocity increased with increasing replacement ratios of FA. The ultrasonic pulse velocity of specimens including FA was higher than that of the control series. The maximum ultrasonic pulse velocity was 1.82 km/s in TPFA40-28.

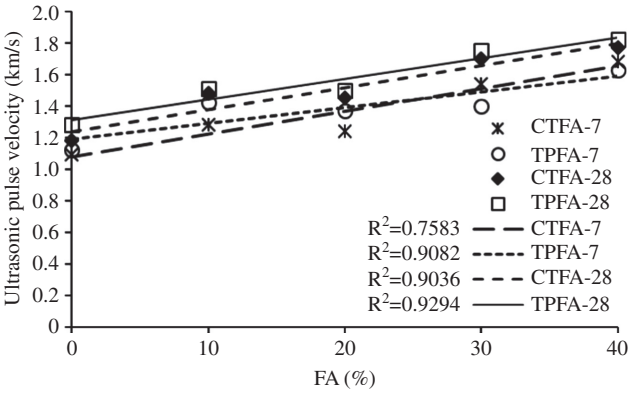


Figure 3 Ultrasonic pulse velocity of specimens.

3.4 Compressive strength

The compressive strength increased with increasing replacement ratios of FA as shown in Figure 4. The compressive strengths of the TPFA series were higher than those of the CTFA series. This can be explained by the

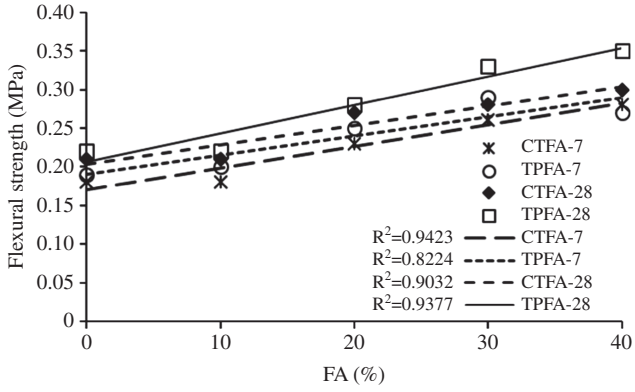


Figure 5 Flexural strength of specimens.

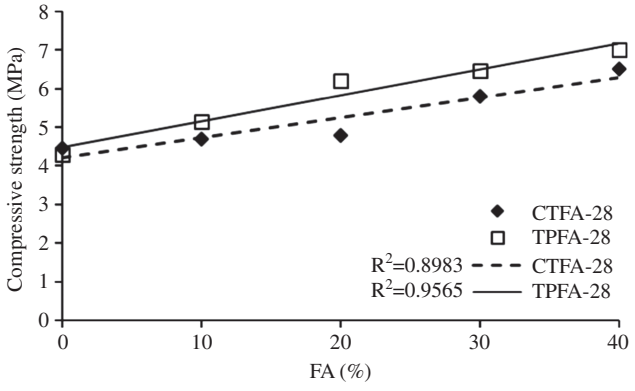


Figure 6 Compressive strength of specimens exposed to freeze-thaw.

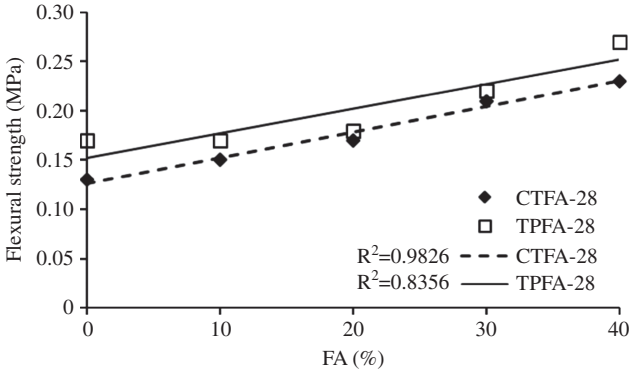


Figure 7 Flexural strength of specimens exposed to freeze-thaw.

lower porous structure of the TPFA series compared to that of the CTFA series. The compressive strengths of specimens cured for 28 days were higher compared to that of specimens cured for 7 days. The compressive strength was 8 MPa in TPFA40-28.

3.5 Flexural strength

The flexural strengths increased with increasing replacement ratios of FA as shown in Figure 5. The flexural strengths of the TPFA series were higher compared to that of the CTFA series due to the porous structure of the CTFA series. The flexural strengths of specimens at the early ages were certainly lower. The flexural strength was 0.35 MPa in TPFA40-28.

3.6 Compressive and flexural strength after freeze-thaw

The compressive and flexural strength increased with increasing replacement ratios of FA despite the deterioration of specimens, as shown in Figures 6 and 7. The flexural and compressive strength of specimens that were exposed to freeze-thaw were lower than those

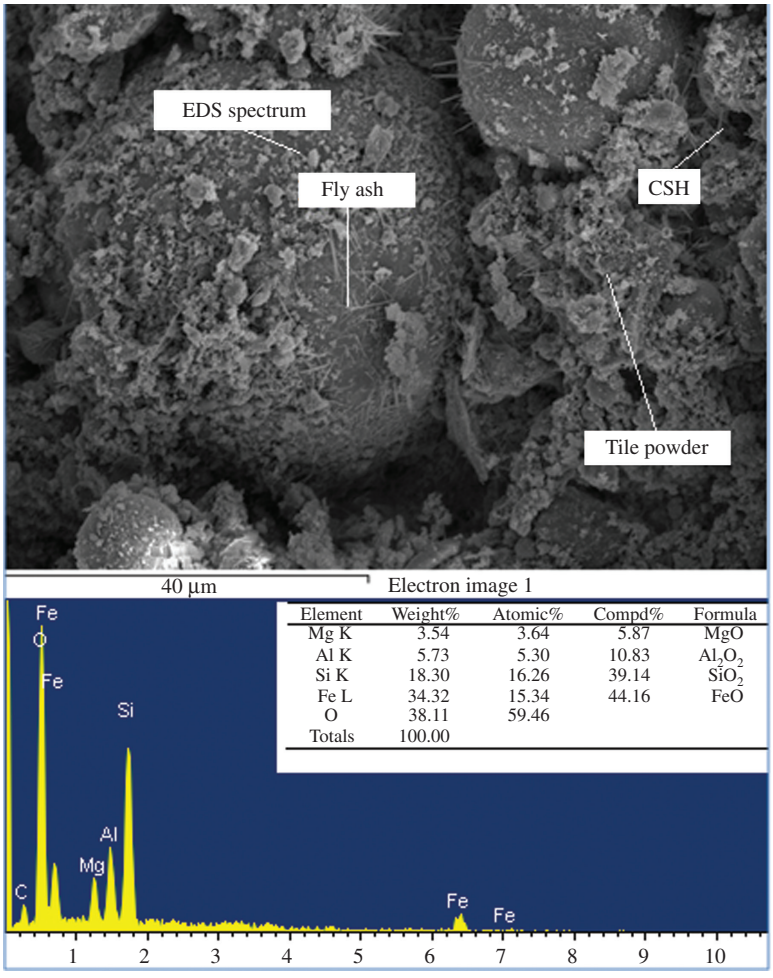
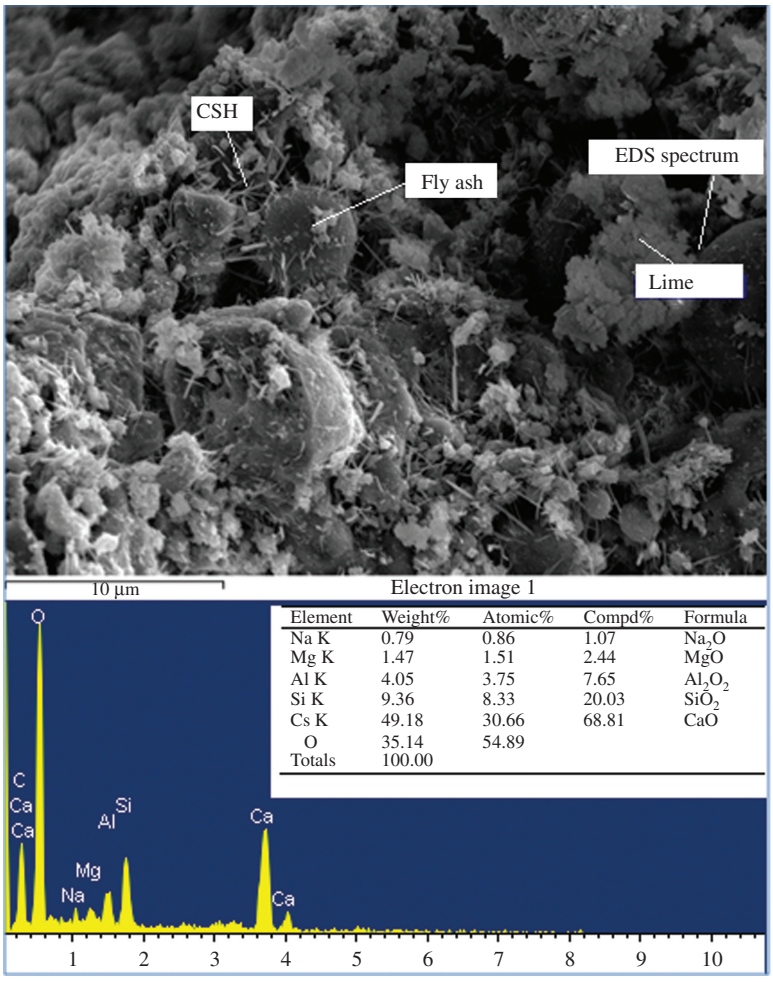


Figure 8 Secondary electron image of FA and TP.



Element	Weight%	Atomic%	Compd%	Formula
Na K	0.79	0.86	1.07	Na_2O
Mg K	1.47	1.51	2.44	MgO
Al K	4.05	3.75	7.65	Al_2O_2
Si K	9.36	8.33	20.03	SiO_2
Cs K	49.18	30.66	68.81	CaO
O	35.14	54.89		
Totals	100.00			

Figure 9 Secondary electron image of FA and lime.

of specimens that were not exposed to freeze-thaw. The maximum compressive and flexural strength after freeze-thaw were 7 and 0.27 MPa, respectively, in TPFA40-28.

3.7 Microstructure, chemical composition, and thermal analysis

In this study, the microstructure and mineralogical composition of TPFA20-28 were examined by SEM and XRD analysis. It is known that fine powder or pozzolanic material improves the hydraulic property of mortars [3, 6]. For this reason, the pozzolanic activity and binding effect of TP-lime, TP-FA, and FA-lime matrices were examined by SEM and TGA. The results indicated that FA-lime had better binding effect compared to TP-lime as shown in Figures 8 and 9. This is explained by the higher CSH formation in FA-lime matrices compared to TP-lime matrices. The rounded shape of FA after hydration, prickly structure around FA particles, and ettringite needles referred to CSH gels were observed in SEM images as shown in Figures 8–10. It was concluded that cohesion between TP and lime was adequate and hydration did not cause deterioration in the structure of FA.

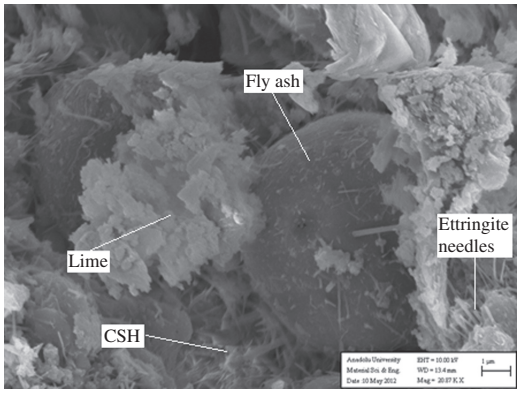


Figure 10 Secondary electron image of CSH formation.

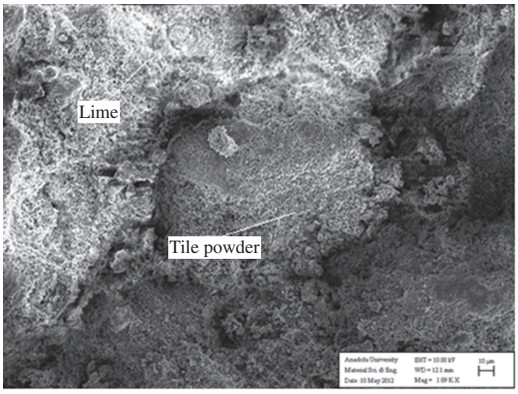


Figure 11 Secondary electron image of slaked lime.

Alumina silicates react with lime in the presence of water to form CSH crystals as shown in Eqs. (1) and (2) [3, 26]. Consequently, crystal formation was examined by SEM analysis as shown in Figures 10 and 11. The crystal structures observed in SEM images were CSH gels that led to higher compressive and flexural strength in mortars. Khorasan mortar is generally composed of SiO_2, CaO, Al_2O_3, and MgO. This was supported by EDS analysis in the study. On the basis of the EDS analysis, TP-lime matrices mostly contained the elements Al, Si, Mg, and Ca as shown in Figures 8 and 9. XRD analysis showed that TP-lime matrices contain feldspar, quartz, calcite, zeolite, hematite, and albite (Figure 12). According to Figure 12, the highest peak referred to the calcite in lime matrix, and the second highest peak referred to the quartz in TP.

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \rightarrow Al_2O_3{\cdot}2SiO_2{+}2H_2O \quad (1)$$

$$Al_2O_3{\cdot}2SiO_2{+}7Ca(OH)_2{+}19H_2O \rightarrow 4CaO{\cdot}Al_2O_3{\cdot}19H_2O{+}3CaO{\cdot}2SiO_2{\cdot}7H_2O \quad (2)$$

In the study, TGA was conducted on TPFA20-28 sample between 30°C and 1000°C to investigate the hydraulic properties of the mortar sample. The weight loss at temperatures between 200°C and 600°C was due to the loss of chemically bound water of hydraulic products, such as CSHs and calcium aluminate hydrates [3, 27]. The weight loss at temperatures higher than 600°C was due to the release of carbon dioxide during the decomposition of carbonates [3, 28]. TGA of mortar sample represented two weight losses at 400–530°C and 570–850°C as shown in Figure 13. The first peak referred to the dehydroxylation of hydraulic products and the second peak referred to the decomposition of carbonated lime [3, 29]. The approximate weight loss of H_2O and CO_2 was 0.076 and 3.262 mg, respectively. The ratio of CO_2/H_2O was 43 and this referred to the hydraulic property of the mortar sample. On the basis of the TGA analysis, the ratio was higher than 10; hence the mortar could be accepted as nonhydraulic [3, 29].

4 Conclusion

On the basis of the experimental results, the mechanical and physical properties of Khorasan mortar and freeze-thaw performance differed depending on curing periods, replacement ratios of FA, and gradation of crushed tiles. In this study, it was observed that the use of FA in Khorasan mortar improved the compressive strength, flexural strength, and binding effect in mortar matrices. Moreover, based on the experimental results, the consistency of fresh mixtures was adequate and the hardened unit weight of specimens was lower compared to that of cementitious mortars.

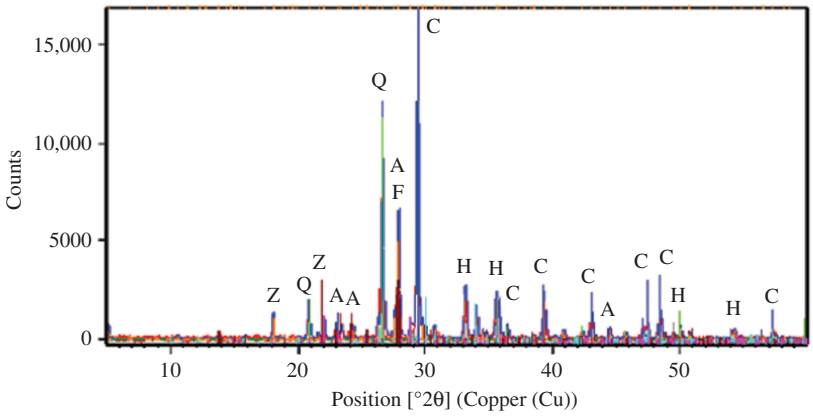


Figure 12 XRD analysis of TPFA20-28 sample. C, calcite; Q, quartz; F, feldspar; Z, zeolite; H, hematite; A, albite.

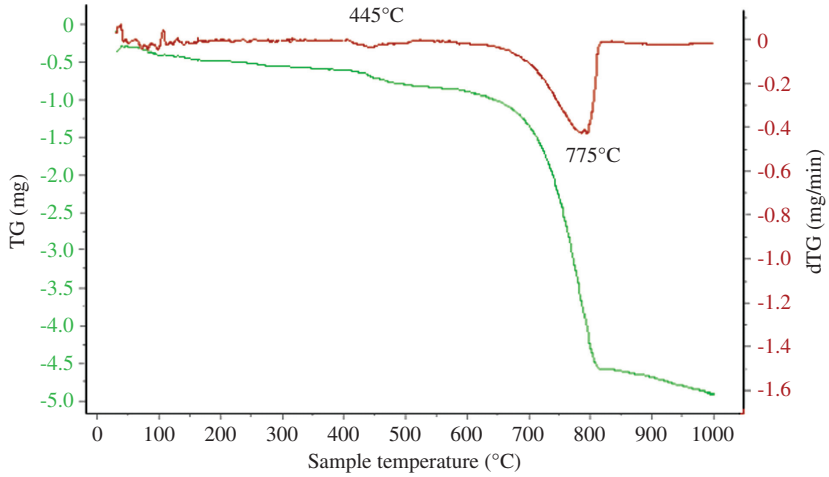


Figure 13 TGA graph of TPFA20-28 sample.

Higher compressive and flexural strengths were observed on the TPFA series compared to the CTFA series. This can be explained by the lower porosity of the TPFA series compared to the CTFA series. On the basis of the mechanical tests, the larger surface area of TP leads to the higher hydraulic property compared to CT. The highest compressive strength and flexural strength were obtained in the specimen TPFA40-28. This specimen also had higher resistance to freeze-thaw effects compared to other specimens. Needless to say, the compressive strength and flexural strength of all specimens decreased with the exposure to freeze-thaw cycles because of parasitic tensile stress. According to SEM analysis, the binding effect between TP and lime matrices was stronger than that of other mortar matrices due to higher CSH formation in crystal structures.

Based on the EDS analysis, the TPFA20-28 sample contains SiO_2, CaO, Al_2O_3, and MgO. According to XRD analysis, the TPFA20-28 sample contains minerals such as calcite, quartz, feldspar, zeolite, hematite, and albite. From the SEM and XRD analysis it is concluded that TP and CT had lower pozzolanic activity.

In this study, industrial waste tiles were used as aggregate after pulverization. In general, industrial tiles are produced by firing at a temperature higher than 900°C; thus, the pozzolanic activity of the TP and CT can be classified as low pozzolanic. The results of thermal analysis and mechanical tests also proved the low pozzolanic activity of TP and CT. In general, compressive strength of <8 MPa leads to the nonpozzolanic activity and nonhydraulic property in brick-lime mortars owing to lower chemically bound water content [1, 3]. This situation was also proved by SEM and TGA in this study.

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