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Characteristics of brick used as aggregate in historic brick-lime mortars and plasters

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Abstract

Mortars and plasters composed of a mixture of brick powder and lime have been used since ancient times due to their hydraulic properties. In this study, raw material compositions, basic physical, mineralogical, microstructural and hydraulic properties of some historic Ottoman Bath brick-lime mortars and plasters were determined by XRD, SEM-EDS, AFM, TGA and chemical analyses. The mineralogical and chemical compositions, microstructures, morphologies and pozzolanicities of the brick powders and fragments used as aggregates in the mortars and plasters were examined to find out the relationship between hydraulic properties of the mortars and the bricks. The characteristics of bricks used in the bath domes were also determined to investigate whether the brick aggregates used in mortar and plasters were prepared from these bricks. The results indicated that the mortars and plasters were hydraulic owing to the presence of crushed brick powders that have good pozzolanicity. The brick powders had high pozzolanicity because they contained high amounts of calcium-poor clay minerals in their raw materials that were fired at low temperatures. On the other hand, bricks used in the domes had poor pozzolanicity with different mineralogical and chemical compositions from bricks used in mortars and plasters. Based on the results of the analysis, it was thought that the bricks manufactured with high amounts of clays were consciously chosen in the preparation of hydraulic mortars and plasters.

Keywords: $Ca(OH)_2$; Mortar; Pozzolan; Calcium–Silicate–Hydrate (C–S–H); Historic brick-lime plaster

1. Introduction

Crushed or finely ground bricks called as Horasan in Turkey, Surkhi in India, Homra in Arabic countries and Cocciopesto in Roman times have been used as aggregates in the manufacturing of lime mortars and plasters since ancient times [1–3]. The mortars and plasters made by mixing crushed bricks with lime set in the presence of water and have high mechanical strength [3]. Due to their setting in water and owing to their high mechanical strength, these mortars and plasters have been used in the construction of aqueducts, bridges, and bath buildings since Roman times.

The raw materials used in the manufacture of bricks are natural clays containing quartz, feldspar and other accessory minerals. The function of clay minerals is to provide plasticity while feldspar acts as a flux to decrease the melting point and quartz is a space filler in the bricks. Bricks are manufactured by first removing coarse stones from the natural clay source before mixing with water. The plastic mixture is then shaped, dried and heated. Heating destroys the crystal structure of clay, which results in pozzolanic amorphous substances like metakaolin when the heating temperature is roughly between 450 and 800 °C depending on the type of clay mineral [4]. At temperatures over 800 °C, pozzolanic activities are lost due to the reduction of surface area and the formation of high temperature mineral phases such as mullite and cristobalite [5].

Amorphous substances are largely aluminosilicates that react with lime to produce calcium silicate hydrate and/or calcium aluminate hydrate at the brick–lime interface and the pores of the bricks. For instance, the amorphous metakaolin ($Al_2O_3.2SiO_2$) derived from the kaolinite ($Al_2O_3.2SiO_2.2H_2O$) in brick reacts with lime ($Ca(OH)_2$) in the presence of water to form calcium

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silicate hydrate ($3CaO.2SiO_2.7H_2O$) and tetracalcium aluminate hydrate ($4CaO.Al_2O_3.19H_2O$) that give the hydraulic character to the mortars and plasters (Eqs. (1) and (2)) [6].

$$Al_2O_3.2SiO_2.2H_2O \rightarrow Al_2O_3.2SiO_2 + 2H_2O \quad (1)$$

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

Formation of these products, in the form of interlocking crystals, improves the strength of the mortars and plasters which, in turn, justifies their use in the construction of many historic buildings since ancient times [7]. The large amount of water on the left side of the reaction Eq. (2) means that these mortars are well suited for extended use in humid environments like historic baths [8].

In the recent works, raw materials compositions, physical, mineralogical and microstructural characteristics of brick-lime mortars in some historic buildings such as in Rhodes, Crete, Venice and Hagia Sofia were determined to understand their technology and to produce compatible repair mortars with the existing ones in masonry structures [7,9–13]. The investigated mortars showed different technologies having binder/aggregate ratios varying from 1/4 to 1/2 in volume. The binders were mostly composed of a high amount of calcite due to the carbonated lime and calcium silicate hydrates and, calcium aluminate hydrates due to hydraulic reaction of lime with the brick aggregates.

It is well known that the use of fine powdered natural or artificial pozzolana increases the hydraulicity of the mortars and plaster owing to their high surface area [3]. But, in some Roman, Byzantine and Ottoman period buildings, coarse brick aggregates which acquire less hydraulic character were used in thick joint mortars [14]. The use of coarse brick aggregates in the thick joint mortars was, however, explained by their roles in influencing deformability and weight of the mortar as opposed to a pozzolanic contribution [14].

Recently, it was proposed that despite the low firing temperatures, historic bricks were not pozzolanic [15,16]. In this study, the pozzolanicity of historic bricks that were used as aggregate in the mortars and plasters of some of the Ottoman baths was studied. The purpose was to find out whether the choice of the bricks had any connection to their pozzolanic activities. Tools like XRD, SEM-EDS, AFM, TGA and chemical analyses were utilized.

Table 1
%Lime/aggregates and particle size distribution of aggregates

Sample	% Lime	% Aggregate	Particle size distribution of aggregates				
			% 1000 μ	% 500 μ	% 250 μ	% 125 μ	<% 125 μ
S-P-1	70	30	17	18	17	20	26
S-P-2	62	38	12	8	24	35	16
S-P-3	50	50	12	22	20	23	22
B-P-1	73	27	16	18	23	21	21
B-P-2	49	51	14	19	16	20	27
O-P-1	44	56	13	21	19	34	13
O-P-2	42	58	17	16	16	22	27
B-M	40	60	23	19	21	16	19

(S: Saray Bath; B: Beylerbeyi Bath; O: Ördekli bath; P: plaster; M: mortar).

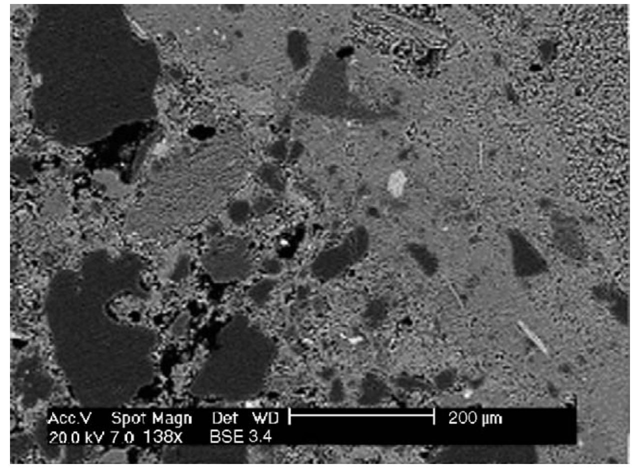

Fig. 1. BSE image of brick aggregates within the mortar matrix. Upper right portion of the picture was the lime binder and the lower left portion was the brick aggregate filler.

2. Materials and method

In this study, seven brick-lime plasters, one dome mortar and three dome bricks were collected from three Ottoman bath buildings constructed in the 14th and 15th century, in Edirne (Saray and Beylerbeyi) and Bursa (Ördekli), Turkey. All samples were sound and in good appearance without any sign of deterioration.

Experimental work consisted of several types of analysis to understand the basic physical properties, microstructural features, and mineralogical and chemical compositions of the mortar and plaster samples. Bulk density and porosity, which are the basic physical properties of the samples, were determined by

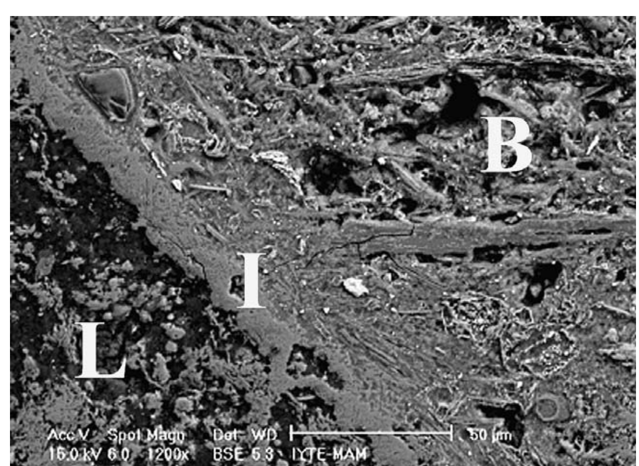

Fig. 2. Backscattered electron image of the interface (I) between the lime matrix (L) and the brick aggregate (B).

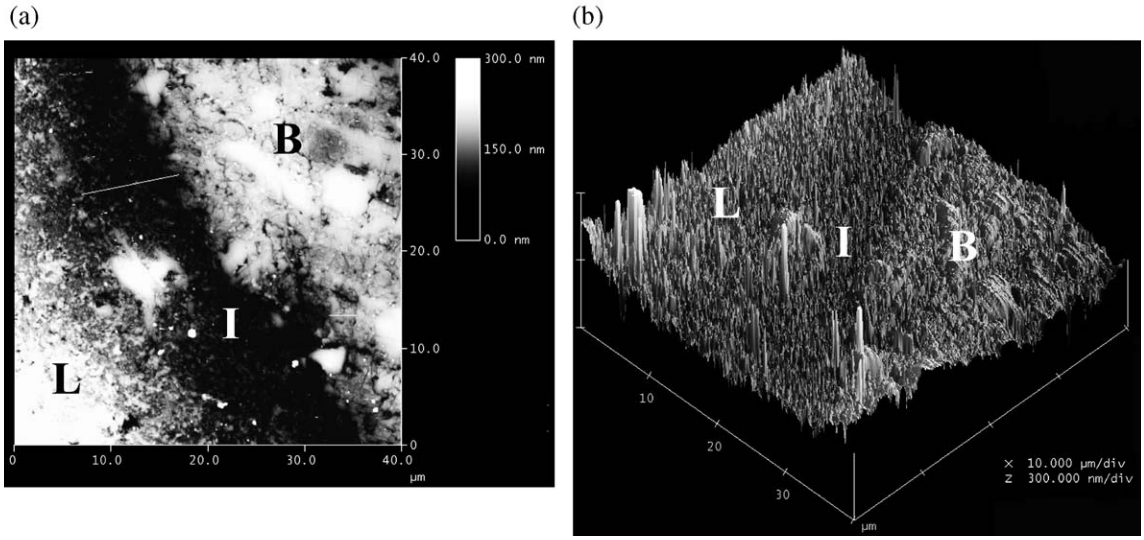

Fig. 3. AFM image showing the thin brick–lime interface (a) and topography (b) of the interface (I) between the mortar matrix (L) and the brick aggregate (B).

using standard test methods [17]. Uniaxial compressive strength (UCS) of the mortars was determined by using point load test apparatus due to the small size of the samples (~2.5 cm.) [18]. Raw materials of the mortars were determined by dissolving their binder in dilute hydrochloric acid and sieving the undissolved brick powder in a standard sieve set [19].

Mineralogical compositions of the mortars, plasters which contained both binder and brick powders and bricks used in the

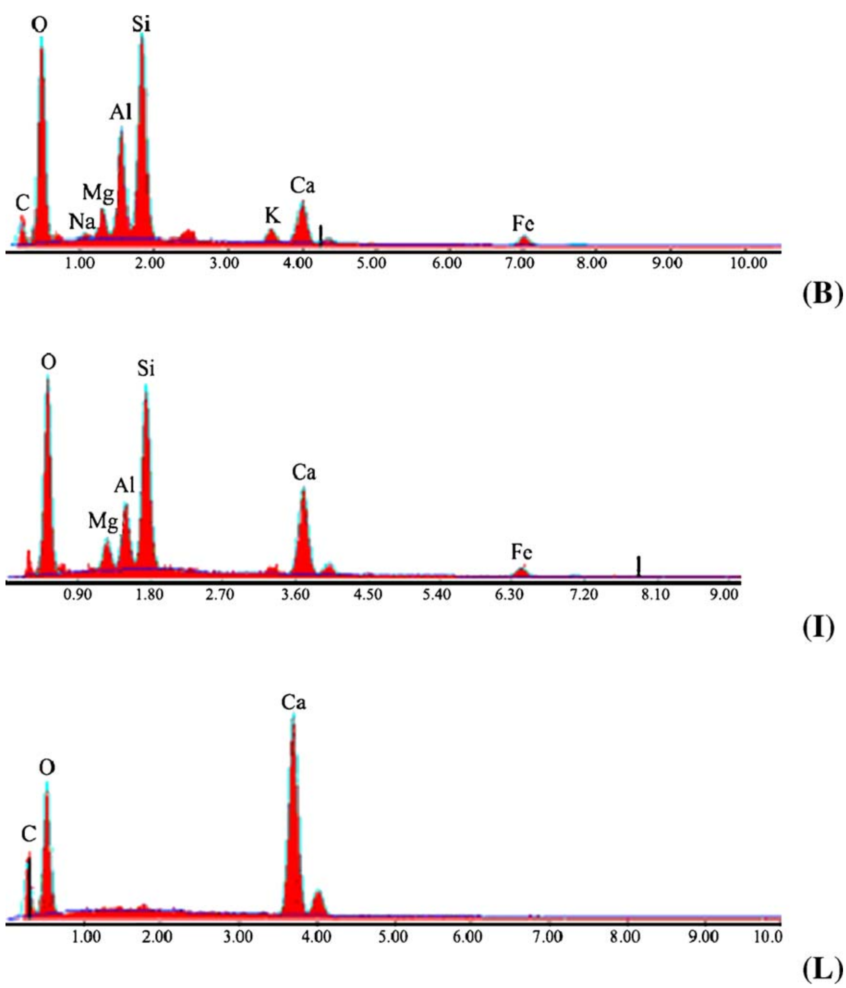

Fig. 4. EDS spectrum of brick aggregates (B), interface (I) and lime matrix (L).

domes were determined by using a Philips X-Pert X-Ray diffraction (XRD). Their morphologies, microstructures and chemical compositions were determined by using Philips XL-30-SFEG model scanning electron microscope (SEM) coupled with EDS (EDAX Co). Characteristics of brick–lime interfaces and their composition were investigated using SEM-EDS and atomic force microscopy (AFM, Digital instruments, MMSPM-Nanoscope 4) on polished sample surfaces.

Hydraulic properties of the mortars and plasters were predicted by determining the weight loss due to chemically bound water of hydraulic products between 200 and 600 °C, and the weight loss due to the carbon dioxide content of the carbonated lime between 600 and 900 °C by using Shimadzu TGA-21 [20]. TGA analysis was also performed on the brick specimens to determine whether they contained clay minerals that did not dissociate during the original firing process.

The pozzolanic activity of the bricks was found by two different methods. In the first method, the differences in electrical conductivities (mS/cm) were measured before and after addition of powdered brick (less than 53 μm) into saturated calcium hydroxide solution [21]. In the second method, brick powder was added to a saturated solution of calcium hydroxide in order to determine the extent of its reaction with calcium hydroxide. The fixation of calcium ions by the bricks was determined after 8, 18 and 30 days by measuring the calcium concentration in the calcium hydroxide solution [22].

Table 2
Percent carbondioxide (CO_2), water (H_2O) and CO_2/H_2O ratios, and compressive strength values of plasters and mortar samples

Samples	%CO_2	%H_2O	CO_2/H_2O	Compressive strength (MPa)
S-P-1	23.2	8.9	2.6	17.63
S-P-2	25.2	6.1	4.1	–
S-P-3	14.7	5.1	2.9	22.0
B-P-1	27.1	4.2	6.5	13.7
B-P-2	18.1	3.6	5.0	–
O-P-1	14.3	3.4	0.2	–
O-P-2	18.6	8.1	2.3	15.68
B-M	10.1	3.9	2.6	10.2

3. Results and discussion

3.1. Characteristics of brick-lime mortars and plasters

Brick-lime mortars and plasters had a stiff and compact appearance. Their density and porosity values were nearly 1.7 g/cm^3 and 38% by volume, respectively. The lime binder and brick aggregate ratios of mortars were around 1/3 by weight and aggregates bigger than 1 mm were the largest fraction of the aggregates. On the other hand, lime binder and brick aggregate ratios of plasters were around 1/2 by weight with fewer large particles (Table 1).

The cohesion between brick aggregates and lime was diffuse and strong in all mortar and plaster matrices (Fig. 1). Interface between lime and brick aggregates was about 10 μm wide that was free from large pores and was composed largely of Ca, Si, and Al elements (Figs. 2 and 3). AFM image (Fig. 3b) shows uniform topography and homogeneous surface without any discontinuity between the lime and brick aggregates in the samples. From the brick aggregates towards the lime matrix, Ca content increased while Si and Al contents decreased (Fig. 4). In the lime matrix, Ca reached its highest content. Hydraulic compounds, such as calcium silicate hydrates and calcium aluminate hydrates at the interface were most likely due to reactions between lime and brick aggregate.

In order to evaluate the hydraulic properties of mortars and plasters, thermal analysis (TGA) was carried out. For this

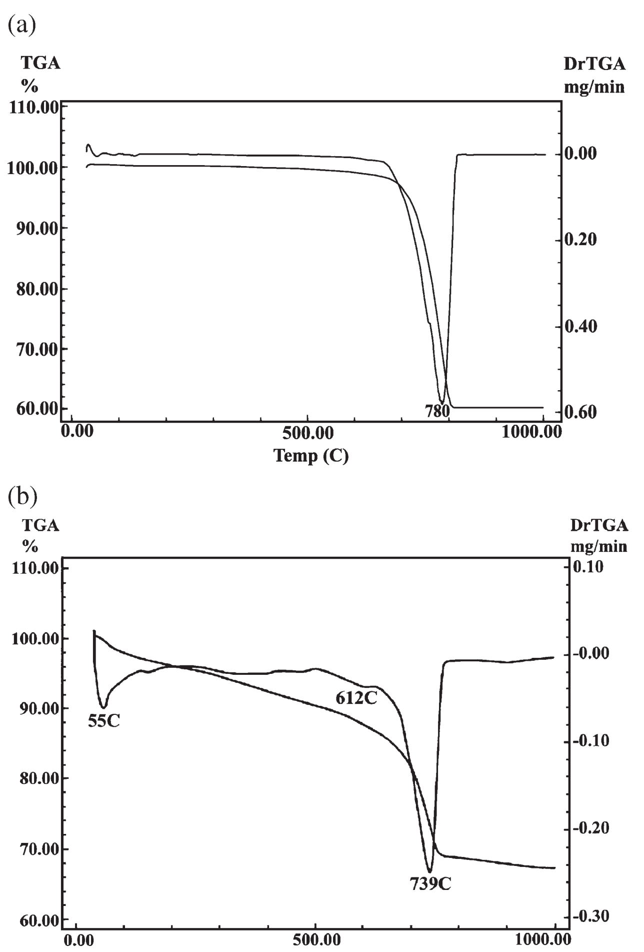

Fig. 5. TGA graph of the binder (a) and the whole brick-lime plaster (b).

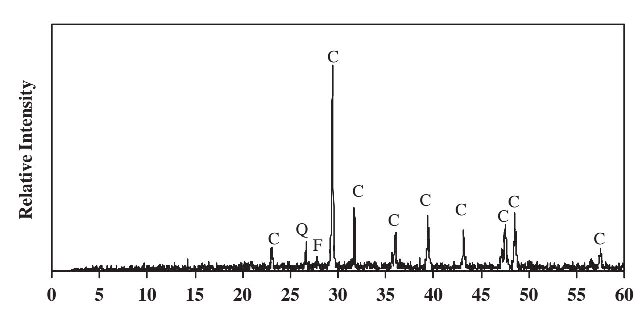

Fig. 6. XRD pattern of the matrix of brick-lime plasters and mortars. C: Calcite, Q: Quartz and F: Feldspar.

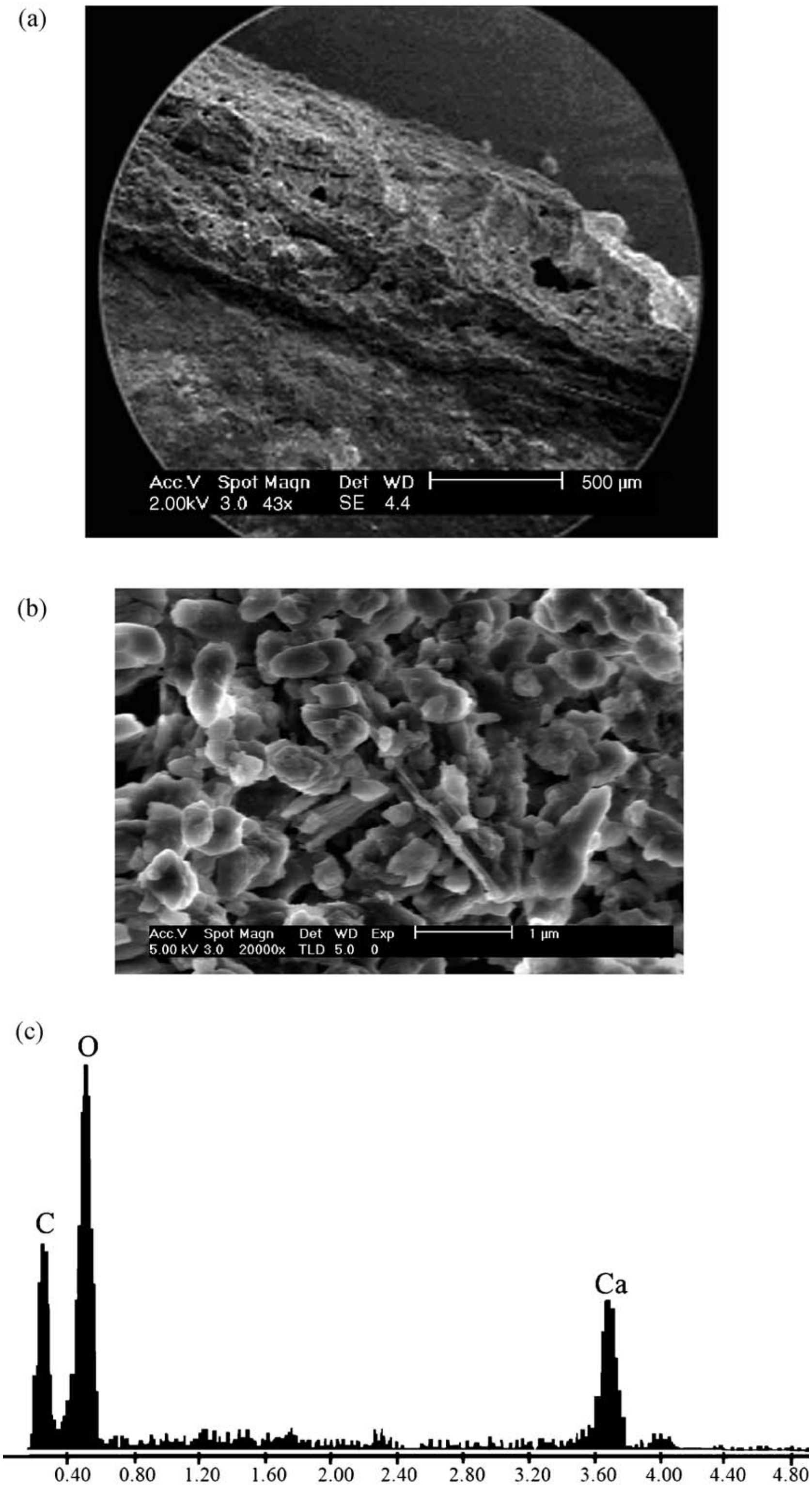

Fig. 7. Secondary electron image (a), submicron crystals (b) and EDS spectrum of the deposited calcite layer on the top layers of the plasters (c).

purpose, percentages of weight losses at 200–600 °C and at temperatures over 600 °C were determined. Weight loss at temperatures of 200–600 °C was mainly due to loss of chemically bound water of hydraulic products, such as calcium silicate hydrates and calcium aluminate hydrates [20]. Weight loss at temperatures over 600 °C was due to CO_2 released during the decomposition of carbonates. When the ratio of CO_2/H_2O was lower than 10, the mortars could be accepted as hydraulic [23].

TGA analysis of mortars and plasters indicated three distinct weight losses around 60 °C, 500–650 °C and 750–870 °C (Fig. 5a,b). The first peak was due to the loss of hygroscopic water, the second peak was probably dehydroxylation of hydraulic products and the third peak was due to the decomposition of carbonated lime.

The CO_2/H_2O ratio of the binders was found to be nearly 40. This indicates that the binder is nearly composed of carbonated lime. On the other hand, the CO_2/H_2O ratio of all plasters and mortars were found to be less than 10 (Table 2), meaning that all mortars and plasters could be regarded hydraulic originating from the reaction of lime with brick powders. The compressive strength values of the mortars were found to be higher than 10 MPa (Table 2). Considering the compressive strength values of more than 9 MPa for hydraulic mortars in the relevant literature, the samples may also be accepted as hydraulic mortars [24].

XRD patterns of the mortar and plaster matrices showed that they were mainly composed of calcite, quartz and feldspar (Fig. 6). Calcite was derived from carbonated lime, while quartz and feldspar were from brick powders. Although the hydraulic characters of the mortars and plasters were found by TGA analysis and indirectly by the mechanical tests, the expected main XRD peaks of calcium silicate hydrate and calcium aluminate hydrate were not observed in the mortar and plaster matrices. This was probably due to amorphous characters of these hydraulic products.

Bath buildings have high-humidity and high temperature environment. Due to the humid and warm conditions of the baths, all plasters contained a white layer of calcite deposits by the subsequent dissolution of carbonated lime determined by XRD on their surfaces and in their pores (Fig. 7a). SEM-EDS analysis indicated that the deposit layers were composed of small sized calcite crystals (Fig. 7b) containing high amounts of calcium oxide over 95% (Fig. 7c).

Although there was calcite deposition, the wall plasters of the baths stood in perfectly good condition. The reason for this phenomenon is the small grain size of the chemically deposited calcite in solution and the subsequent build up of a very dense structure.

3.2. Characteristics of bricks

The densities and porosities of bricks used in the domes were found to be nearly similar with the ones in the mortars and plasters. Density and porosity values were between 1.7 and 1.8 g/cm^3 and 33–37% by volume, respectively.

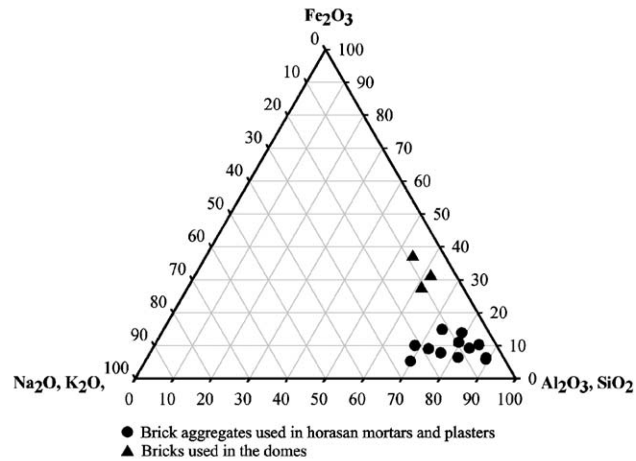

Fig. 9. Compositions of the bricks.

XRD patterns of all bricks showed that they were composed of quartz (SiO_2), being the main component, potassium feldspar ($KAl_2Si_2O_5(OH)_4$), sodium feldspars ($NaAlSi_3O_8$) and biotite ($KMg_3AlSi_3O_{10}(OH)_2$). However, in the XRD patterns of brick aggregates in mortars and plasters, a diffuse band between 20° and 30°2θ was observed (Fig. 8). This band probably showed the presence of amorphous substances derived from the high amounts of calcined clay minerals [5]. This finding suggested that the brick aggregates in the mortars and plasters were manufactured differently by using materials of high clay content. The oxide composition analysis of brick aggregates and bricks used in domes by EDS indicated that all the bricks were mainly composed of a high amount of SiO_2, Al_2O_3 and moderate amount of Fe_2O_3, Na_2O and K_2O (Fig. 9). However, the amounts of Fe_2O_3 in all bricks used in the domes of the baths were found to be higher than that of all bricks used in mortars and plasters. The absence of detectable calcium by SEM-EDS analysis (Fig. 9) showed that clay minerals containing low amounts of Ca were used as raw materials in the manufacture of all brick aggregates and the brick used in domes.

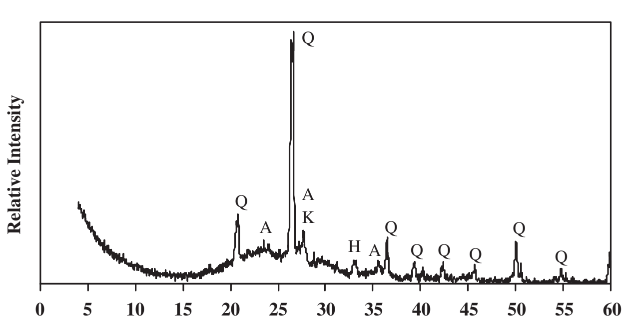

Fig. 8. A typical XRD pattern of the brick aggregates. A: Albite, Q: Quartz, K: Feldspar and H: Hematite.

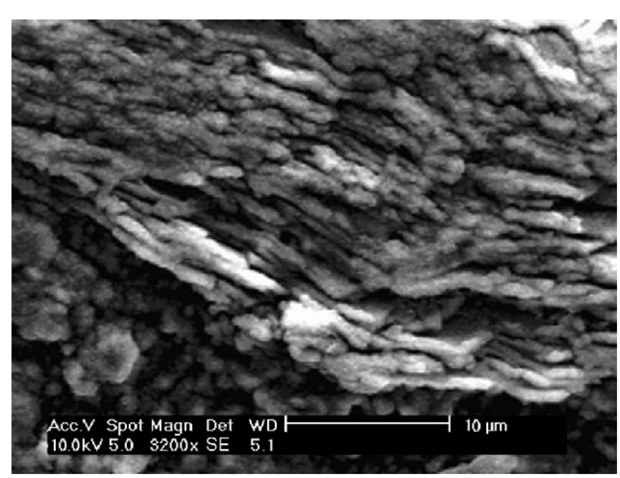

Fig. 10. Secondary electron image of amorphous substances in brick aggregates.

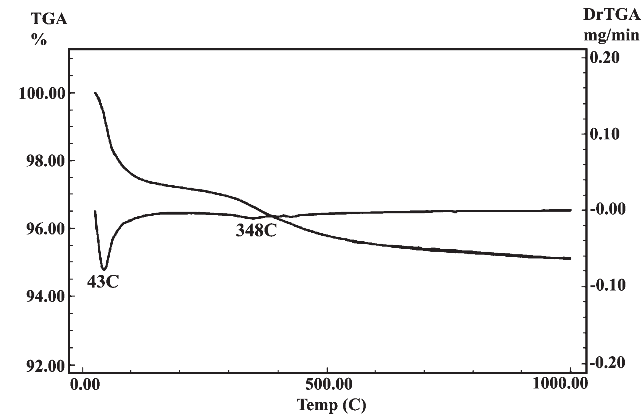

Fig. 11. TGA graph of the brick aggregates used in the mortars and plasters.

Both bricks were probably manufactured from locally available raw material sources in the region. However, the lower iron content in bricks in mortars and plasters may be explained by their relatively higher clay content that has less iron. The observation of a diffuse band between 20° and 30° in the XRD patterns of brick aggregates suggests the use of high amounts of clay minerals in their production.

Microstructure of brick aggregates showed little vitrification (Fig. 10) suggesting a low heating temperature (T<950 °C). XRD analysis results also supported this finding. Absence of high temperature products of dissociated clay minerals like mullite in the XRD diffraction patterns showed that firing temperatures did not exceed 950 °C.

Thermal analysis (TGA) was carried out in order to evaluate whether the firing of bricks was carried out until the clay minerals dehydroxylated. TGA analysis of all bricks indicated two distinct weight losses around 50 °C, and between 350 and 400 °C (Fig. 11). The sharp first peak was due to the loss of hygroscopic water, while the weak second peak was possibly due to organic materials. The absence of clay dehydroxylation peaks indicated that all clay minerals lost their chemically bound water during firing of the brick aggregates and the bricks used in domes.

The pozzolanic activity of the bricks was determined by following the reaction between lime and bricks by electrical conductivity measurements and by determination of calcium concentration in the calcium hydroxide solution.

Pozzolanic activity measurements by electrical conductivity measurements were found to be more than 2 mS/cm in bricks used in mortars and plasters which can be regarded as good pozzolan (Fig. 12) [21]. However, the values of pozzolanicity in the bricks used in the construction of domes were relatively lower than the bricks used in mortars and plasters. Similarly, in the second method, the fixation of calcium ions by the brick aggregates in all mortars and plasters in saturated lime solution after 30 days was found relatively higher than for the dome bricks (Fig. 13). These results showed that the brick aggregates of all mortars and plasters had good pozzolanicity but the bricks used as construction materials demonstrated variable pozzolanicity. Similar results have also been found in studies carried out on the bricks used in historic Ottoman bath plasters and domes in Urla region, Turkey [25].

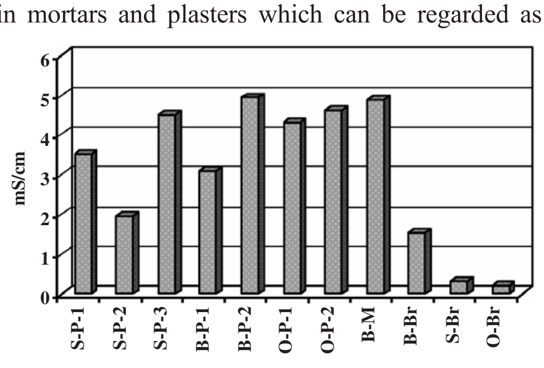

Fig. 12. Pozzolanic activity values of the bricks.

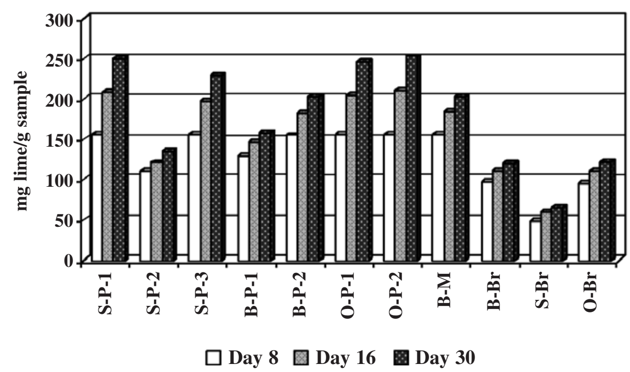

Fig. 13. Amount of lime that reacted with brick powder after 8, 16 and 30 days.

The mineralogical, chemical and pozzolanic activity analysis results show that the bricks used in mortars and plasters were not the same as the bricks used in domes. These results may indicate that the pozzolanic bricks were intentionally chosen for the manufacturing of hydraulic mortars and plasters.

4. Conclusions

Historic brick-lime mortars and plasters used in the Ottoman bath buildings have reached the present without significant deterioration. This shows that brick-lime mortars and plasters were ideal cementing materials, especially for the moist and hot environment of the historic bath buildings. Their utility for use in the moist environment may be explained by their hydraulic characteristics due to the reaction products of lime binder with brick aggregates at the brick–lime interface and the pores of the bricks. These products provide strong adhesion bonds, which make the mortars and plasters durable and stiff.

The bricks used as aggregates in the mortars and plasters have good pozzolanicity mainly derived from their amorphous clay mineral dissociation products. On the other hand, bricks used in the construction of the domes of the bath buildings have poor pozzolanicity due to less amount of amorphous materials. All bricks were little vitrified and did not contain high temperature products like mullite, suggesting low firing temperatures.

These results may indicate that the pozzolanic bricks were particularly chosen for the manufacturing of hydraulic mortars and plasters. As a result of this study, bricks used in the manufacturing of new intervention brick-lime mortars and plasters must have a high amount of clay minerals, and must be fired at low temperatures if they are lean in natural pozzolans.

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References

[1] M.S. Akman, A. Güner, I.H. Aksoy, The history and properties of khorasan mortar and concrete, Turkish and Islamic Science and Technology in the 16th Century, İTÜ Research Center of History of Science and Technology, (I), İstanbul (1986) 101–112.

[2] R. Spence, Lime and Surkhi manufacture in India, Appropr. Technol. 1 (4) (1974) 6–8.

[3] F.M. Lea, Investigations on pozzolanas, Building Research, Technical Paper No.27, 1940, pp. 1–63.

[4] C. He, B. Osbaeck, E. Makavicky, Pozzolanic reactions of six principal clay minerals: activation, reactivity assessments and technological effects, Cem. Concr. Res. 25 (8) (1995) 1691–1702.

[5] L. Sujeong, Y.J. Kim, H.S. Moon, Phase transformation sequence from kaolinite to mullite investigated by an energy-filtering transmission electron, J. Am. Ceram. Soc. 10 (1999) 2841–2848.

[6] W. Prince, G. Castanier, J.L. Giafferi, Similarity between alkali - aggregate reaction and the natural alteration of rocks, Cem. Concr. Res. 31 (2001) 271–276.

[7] A.S. Moropoulou, G. Çakmak, A. Biscontin, E. Bakolas, E. Zendri, Advanced Byzantine cement based composites resisting earthquake stresses: the crushed brick-lime mortars of Justinian's Hagia Sophia, Constr. Build. Mater. 16 (2002) 543–552.

[8] H. Böke, S. Akkurt, Ettringite formation in historic bath brick-lime plasters, Cem. Concr. Res. 33 (2003) 1457–1464.

[9] A. Güleç, T. Tulun, Physico-chemical and petrographical studies of old mortars and plasters of Anotolia, Cem. Concr. Res. 27 (2) (1997) 227–234.

[10] A. Moropoulou, T.h. Tsiourva, K. Bisbikou, G. Biscontin, A. Bakolas, E. Zendri, Hot lime technology imparting high strength to historic mortars, Constr. Build. Mater. 10 (1996) 151–159.

[11] A. Moropoulo, A. Bakolas, K. Bisbikou, Physico-chemical and cohesion bonds in joint mortars imparting durability to the historic structures, Constr. Build. Mater. (14) (2000) 35–46.

[12] A. Bakolas, G. Biscontin, A. Moropouluo, E. Zendri, Characterization of structural Byzantine mortars by thermogravimetric analysis, Thermochim. Acta 321 (1998) 151–160.

[13] G. Biscontin, M.P. Birelli, E. Zendri, Characterization of binders employed in the manufacture of Venetian historical mortars, J. Cult. Herit. 3 (2002) 31–37.

[14] G. Baronia, L. Binda, N. Lombardini, The role of brick pebbles and dust in conglomerates based on hydrated lime and crushed bricks, Constr. Build. Mater. 11 (1997) 33–40.

[15] G. Baronia, L. Binda, Study of the pozzolanicity of some bricks and clays, Constr. Build. Mater. 11 (1997) 41–46.

[16] H. Böke, S. Akkurt, B. İpekoğlu, Investigation of the pozzolanic properties of bricks used in horasan mortars and plasters in historic buildings, Key Eng. Mater. 264–268 (2004) 2399–2402.

[17] RILEM, Tests defining the structure, Mater. Const. 13 (1980) 73.

[18] N. Brook, The equivalent core diameter method of size and shape correction in point load testing, Int. J. Rock Mech. Min. Sci. Geomech. Abstr. 22 (1985) 61–70.

[19] H. Jedrzejevska, Ancient mortars as criterion in analysis of old architecture, Proceedings of the ICCROM Symposium on Mortars, Cements and Grouts Used in the Conservation of Historic Buildings, ICCROM, Rome, 1981, pp. 311–329.

[20] A. Bakolas, G. Biscontin, V. Contardi, E. Franceschi, A. Moropoulou, D. Palazzi, E. Zendri, Thermoanalytical research on traditional mortars in Venice, Thermochim. Acta 269/270 (1995) 817–828.

[21] M.P. Luxan, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural products by conductivity measurements, Cem. Concr. Res. 19 (1989) 63–68.

[22] E. Liebig, E. Althaus, Pozzolanic activity tuff and suevite: effects of calcination, Cem. Concr. Res. 28 (1998) 567–575.

[23] A. Moropoulou, A. Bakolas, K. Bisbikou, Investigation of the technology of historic mortars, J. Cult. Herit. 1 (2000) 45–58.

[24] R. Livingston, Materials analysis of the masonry of the Hagia Sophia Basilica, in: C.A. Brebbia, R.J.B. Frewer (Eds.), Structural Repair and Maintenance of Historic Buildings, Computational Mechanics Publications, Southampton, 1993, pp. 15–32.

[25] E. Uğurlu, Characterization of horasan plasters from some Ottoman baths in İzmir", Master's Thesis, İzmir Institute of Technology, İzmir, 2005.