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Evaluation of heat treated clay for potential use in intervention mortars

Meral Budak [a], Sedat Akkurt [a,*], Hasan Böke [b]

[a] Department of Mechanical Engineering, Izmir Institute of Technology, 35430, Urla-Izmir, Turkey
[b] Department of Architectural Restoration, Izmir Institute of Technology, 35430, Urla-Izmir, Turkey

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ABSTRACT

In this study, raw material compositions, basic physical, mineralogical, microstructural and hydraulic properties of lime mortars used in two selected historic buildings were determined by XRD, SEM-EDS and TGA analyses. The results showed that the mortars were hydraulic due to the use of pozzolanic aggregates. Taking into account the hydraulic characteristics of mortars due to the use of pozzolanic aggregates, the possibility of obtaining hydraulic mortars by using pozzolanic aggregates produced from heated commercial clays was investigated. For this purpose, four clay samples used in the ceramic industry in Turkey were heated at varying temperatures of 400, 450, 500, 550, 600, 800, and 1200 °C with a heating rate of 10 °C/min. Pozzolanic properties of heated clay samples were determined. The results showed that commercial clays studied are well suited for use as pozzolanic aggregates when they are heated between 500 and 700 ºC. This is also confirmed by testing the compressive strengths of the three month aged laboratory-produced mortars that contained thermally treated clay (at 600 °C) as pozzolanic aggregates. Compressive strength of this mortar was around 5 MPa which is satisfactorily high.

1. Introduction

Mortars, produced by mixing binder and aggregates, have been used for bedding, jointing and rendering brickwork and stonework. The oldest mortar used for building was mud, and is still used in many countries throughout the world. In ancient Egypt, mud mortar was used with sun-dried bricks and later gypsum was used as binder in the brick vaults of monumental buildings (Davey, 1961). Lime mortars were commonly used in buildings from Greek times through the beginning of the 19th century (Vendrell-Saz et al., 1996). They are primarily composed of lime as binder and aggregate as filler material.

Lime is produced by calcination of limestone to convert carbonate into oxide (quicklime). This oxide when mixed with water transforms into the hydroxide of calcium. Aggregates generally comprise a large part of the volume of lime mortar and the characteristics of the aggregates chosen are critical for the performance of the mortar. Aggregates can be classified as inert aggregates and pozzolanic aggregates. Inert aggregates do not react with lime. However, the pozzolanic aggregates are active and react with lime in the presence of water (Davey, 1961). Pozzolanic aggregates may be divided into two separate groups; those consisting of natural pozzolans and those of artificial pozzolans (Lea, 1940; Cowper, 2000; Moropoulou et al., 2004). Natural pozzolans include such materials as some diatomaceous earths, opaline, cherts, shales, tuffs and volcanic ashes. The artificial pozzolans are mainly products obtained by the treatment of natural materials such as clays, shales and fly-ash (Lea, 1940). The most common artificial pozzolan is obtained by the heat treatment of clay. The characteristics of clay are therefore important to have an idea about its pozzolanic character. The loss of combined water in the structure of clay leads to destruction of the crystal structure after thermal treatment. The silica and alumina transform into an amorphous state (Baronia and Binda, 1997; Charola and Henriques, 1999). When they are mixed with lime and water, they can produce pozzolanic reactions. Therefore, the determination of the temperature range where the clay turns into an unstable amorphous state is very important.

Determination of lime mortar characteristics for conservation works of historic buildings became an important task in the second half of the 20th century due to the extensive damage of cement mortars used in historic buildings (Rodriguez-Navarro et al., 1998). Historic buildings should be conserved by original materials and intervention materials used in the restoration must be compatible with original ones. Hence, the characterization of building materials plays an important role in restoration works of historic buildings.

The aim of this work is the characterization of aggregates that were used in historic lime mortars collected from Çukur Hamam and Hacet Mescidi, and according to the results, to determine the characteristic of clay samples which will be used as pozzolanic aggregate for the production of intervention mortars that are compatible with the original ones.

* Corresponding author. Tel.: +90 232 750 6705; fax: +90 232 750 6701.
E-mail address: sedatakkurt@iyte.edu.tr (S. Akkurt).

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2. Experimental procedure

2.1. Characterization of lime mortars and their aggregates

In this study, lime mortars were collected from two buildings which were both constructed in 14th century. These buildings are known as Çukur Hamam (Ç) and Hacet Mescidi (H) and are located in the city of Manisa in western Turkey (Fig. 1). Table 1 shows codes and locations of all samples. Basic physical properties, microstructural features, mineralogical and chemical compositions of the mortars were determined by XRD and SEM-EDS. TGA analysis was done in a separate study by one of the authors (Budak, 2005).

Bulk density and porosity of the mortars were determined by measuring the dry, water saturated under vacuum, and hydrostatic weights of samples (RILEM, 1980). Lime and aggregate ratios of mortars were determined by dissolving the carbonated lime in mortars with dilute hydrochloric (HCl) acid (Jedrzejevska, 1981; Middendorf and Knöfel, 1990).

Pozzolanic activities of the aggregates (less than 53 µm size) were determined by measuring the differences in electrical conductivities (mS/cm) before and after addition of the samples into saturated calcium hydroxide solution (Luxan et al., 1989). The mineralogical compositions, microstructures and chemical compositions of aggregates were determined by XRD and SEM-EDS analyses. Philips X-Pert Pro X-Ray Diffractometer (CuKα radiation) in the range of 2–70° and Philips XL 30S FEG Scanning Electron Microscope (SEM) coupled with X-Ray Energy Dispersive System (EDS) were used in the analyses (Table 2).

Table 1
Identification codes of collected samples and their description.

Identification codes	Description
Ç-M-BB1	Brick masonry mortar (dome starting point)
Ç-M-BB2	Brick masonry mortar (dome)
Ç-M-SS	Stone masonry mortar (entrance door)
Ç-M-BB3	Brick masonry mortar (dome)
H-M-BB	Brick masonry mortar (dome)
H-M-SS	Stone masonry mortar (wall)

Ç: Çukur Haman (bath), H: Hacet Mescidi (Mosque), BB: mortar samples from two layers of brick, SS: mortar sample from two layers of stones and M: mortar.

Table 2
The commercial codes of clay samples.

Codes	K-31	K-103	K-244	K-261
Source	Tamsa Seramik A.Ş	Yüksel Seramik A.Ş	Kalemaden A.Ş	Kalemaden A.Ş

2.2. Heat treatment of commercial clays

In this study, the possibilities of producing pozzolanic aggregates by calcination of some commercial clays were investigated. For this

Fig. 1. Map of Turkey showing the location of Manisa.

Table 3
The mixing ratios of binders, aggregates and pozzolans used in preparation of mortar.

Mortar no.	Binder aggregate ratio (g)	Pozzolan/aggregate ratio (g)		
		K-244 (25 °C)	K-244 (600 °C)	K-244 (1000 °C)
1	1/3	1/2		
2	1/3		1/2	
3	1/3			1/2

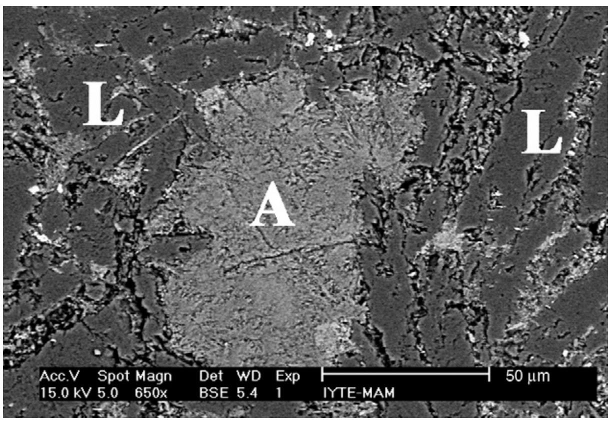

Fig. 2. BSE image showing good adhesion between aggregates(A) and lime(L).

purpose, some commercial clays used in the ceramics industry in Turkey were obtained (Table 3). The chemical compositions of clay samples were determined by SEM-EDS analysis. Clay samples were heated at varying temperatures of 400, 450, 500, 550, 600, 800, and 1200 °C with a heating rate of 10 °C/min. Pozzolanic properties of heated samples (less than 53 µm size) were determined by measuring the differences in electrical conductivities (mS/cm) before and after addition of the samples into saturated calcium hydroxide solution (Jedrzejevska, 1981).

2.3. Preparations of intervention mortars and their uniaxial compressive strengths

K-244 sample was used as pozzolanic aggregate in the preparation of intervention mortars. The binder (lime) to standard sand aggregate ratios were 1:3. Pozzolan additions were made to these mixes in such proportions to obtain pozzolan/aggregate ratios of 1/2 (Table 3).

Mortar mixtures were prepared by following the procedure outlined in ASTM standard (ASTM C109, 2005). The commercial hydrated lime used in preparation of mortar was supplied by Öztüre Kimtaş A.Ş Izmir. The graded standard aggregates were supplied from Çimentaş A.Ş Izmir. Mortar mixtures were prepared by using a Kitchenaid® mini mixer (5lt). After the mixing procedure the samples were cast in cylindrical molds made from commercially available PVC pipes ($R = 5$ cm, $h = 5$ cm). ASTM C593 standard was used for storage of the mortar mixtures (ASTM C593, 2005). After 3 months of storage at 23 ± 2 °C at 95 to 100% relative humidity, their uniaxial compressive strength values (UCS) were determined by using a Shimadzu AG-I Mechanical Test Instrument.

3. Results and discussion

3.1. Properties of lime mortars and aggregates

Density values of stone and brick masonry mortar samples collected from Çukur Hamam and Hacet Mescidi were 1.8 and 1.9 g/cm^3, and porosity values were 34 and 29% by volume, respectively. Density and porosity values of the mortar samples were in a similar range with some

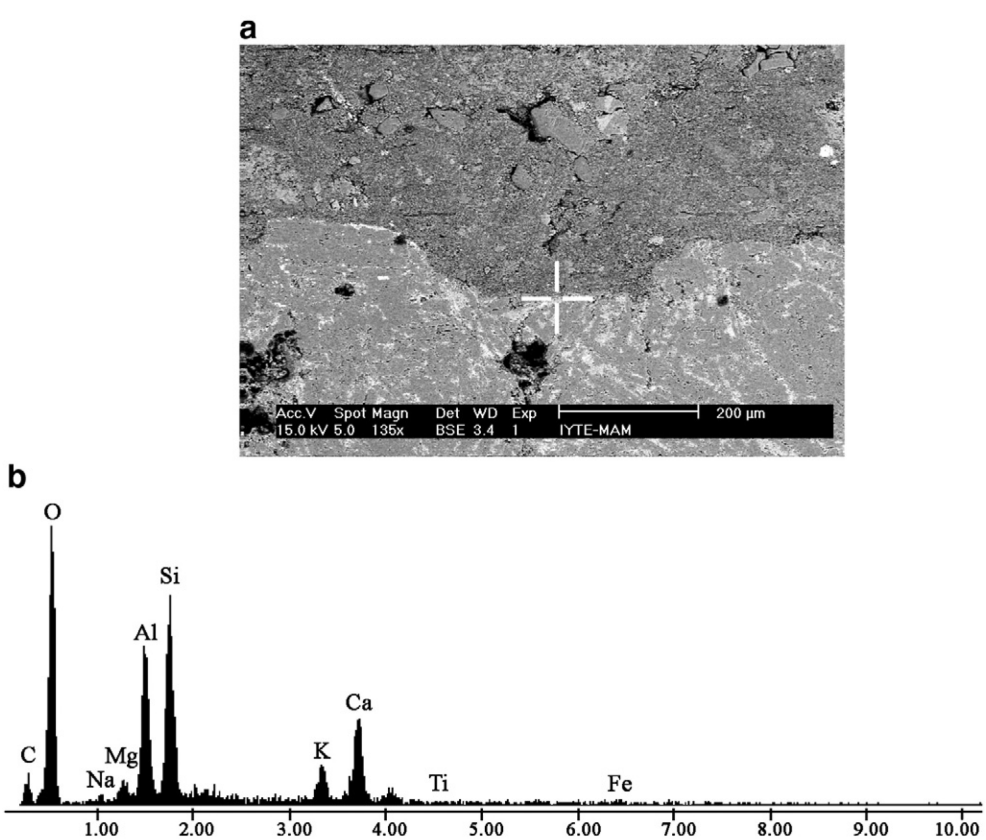

Fig. 3. BSE image (a) and EDS spectrum (b) of the interface between lime and the aggregate surface.

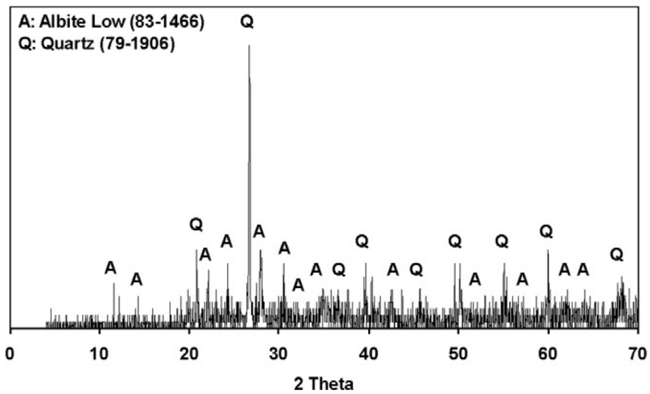

Fig. 4. XRD pattern of the fine aggregates used in brick masonry mortar of C-M-BB2.

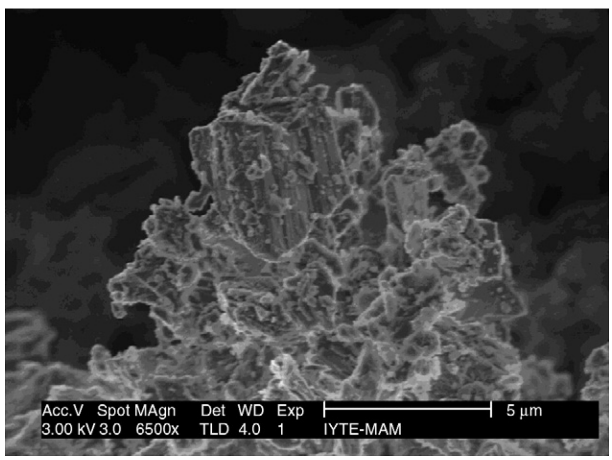

Fig. 5. SE (secondary electron) image of fine aggregates.

other historic lime mortars from different periods of time (Moropoulou et al., 2004; Böke et al., 2006).

Lime/aggregate ratios of the mortars samples ranged from 1:2 to 1:4. Stone masonry mortars of the structures presented high ratios of lime when compared with the brick masonry mortars. Aggregate particle sizes that are greater than 1180 µm composed the largest portion of the total aggregates. These values were in similar ranges to mortars and plasters used in some historic structures (Moropoulou et al., 2000; Bakolas et al., 1998).

The mortars were stiff, hard and compact due to strong cohesion between aggregates and lime (Fig. 2). The aggregates were mostly semi-rounded and porous permitting strong adherence to the lime. Aggregate-lime interfaces were composed largely of calcium, silicon and aluminum (Fig. 3). This may indicate the formation of hydraulic compounds produced by the reaction of pozzolanic aggregates with lime.

The hydraulicity of the mortars was evaluated by thermo gravimetric analyses (TGA) in a previous study by the authors. These analyses indicated that the weight loss between 200 °C and 600 °C was nearly 2.2% and weight loss over 600 °C was 12.9% (Budak, 2005). It has been estimated that if the CO_2/water ratio is between 1 and 10 in a mortar, it can be regarded as a hydraulic mortar. The CO_2/water ratios for mortars were less than 10; hence they were classified as hydraulic mortars (Moropoulou et al., 2000).

3.2. Properties of aggregates used in mortars

The XRD analyses of fine aggregates of mortar samples collected from Çukur Hamam and Hacet Mescidi showed that they were all composed of quartz and some albite (Fig. 4). A broad band indicating the presence of amorphous materials (Sujeong et al., 1999) could be observed between 20 and 30° in XRD patterns (Fig. 4). Therefore, it can be said that there are amorphous materials in the structure of fine aggregates.

Semi quantitative SEM-EDS analysis revealed that the main component in fine aggregates was silica (SiO_2), which varied in the range of 73–85%. The second component of fine aggregates was alumina (Al_2O_3) that varied in the range of 6–10%, and the third important component was iron oxide (Fe_2O_3) which varied in the range of 1–3% (Budak, 2005).

The crystals of fine aggregates had sharp edges (Fig. 5) that caused a high surface area, which was effective for pozzolanic reaction kinetics between lime and fine aggregate. Fine aggregates adhered well to mortar matrices via pozzolanic reaction products, which improve the mechanical strength of mortar. Such mortars are known as hydraulic mortars which maintain strength under water.

Pozzolanic activities of the aggregates (<53 µm) were obtained in the range of 1.71–7.23 mS/cm (Fig. 6). According to Luxan's classification of pozzolanicity (Luxan et al., 1989), the changes in electrical conductivity of calcium hydroxide solution before and after addition of pozzolanic material are classified as; good pozzolan when more than 1.2 mS/cm, variably pozzolan when 1.2–0.4 mS/cm and non-pozzolanic when less than 0.4 mS/cm. Measurement results in this study concluded that all aggregates could be classified as good pozzolans.

According to the results of the XRD, SEM-EDS and pozzolanic activity analyses, the fine aggregates can be characterized as pozzolanic aggregates formed from quartz and albite and amorphous materials, containing high amounts of silica and alumina with a geometry of sharp

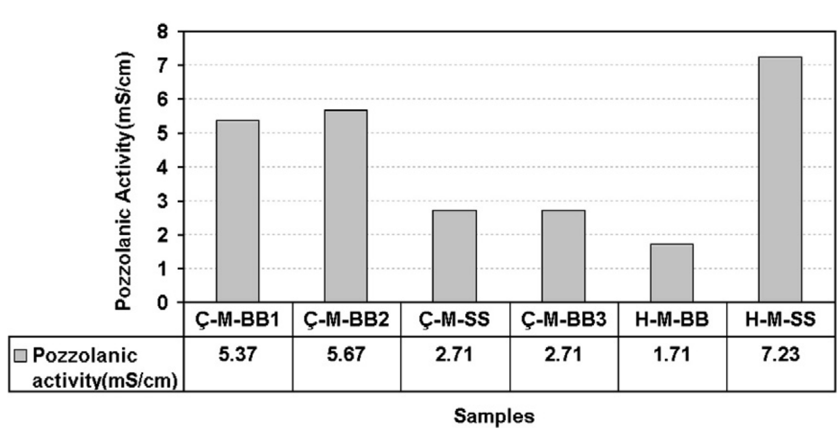

Fig. 6. Pozzolanic activity values of fine aggregates (<53 µm).

Table 4
Chemical composition of clay samples (EDS).

Oxides (%)	K-31	K-103	K-244	K-261
Na_2O	0.9	0.9	1.1	1.2
MgO	1.2	1.6	1.6	1.4
Al_2O_3	41.4	33.3	33.1	40.8
SiO_2	52.6	56.5	58.7	53.4
K_2O	2.4	2.6	2.4	0.4
CaO	0.1	0.4	0.4	0.2
TiO_2	0.3	1.3	1.0	1.0
Fe_2O_3	1.1	3.4	1.6	1.6

edges. The aggregate that will be used in production of intervention mortar should have similar properties to the fine aggregates.

3.3. Properties of heat treated clays

SEM-EDS analysis showed that the clay samples had oxide contents in the range of 52–58% for SiO_2, 33–41% for Al_2O_3, 0.9–1.2% for Na_2O and 0.4–2.6% for K_2O (Table 4). Their pozzolanic activity (PA) values at different temperatures are given in Fig. 7 (Budak et al., 2003). The results show that most clay samples were not sufficiently pozzolanic before heat treatment. The maximum PA values were obtained for the K-103 sample while the lowest PA was shown by the K-31 sample before heat treatment. High pozzolanic activity of K-103 sample can be attributed to natural pozzolans in the structure of this sample. The pozzolanic activity measurement at different temperatures showed that the maximum pozzolanic activity values for all samples were obtained in the range of 550–600 °C. This result was expected because the clay crystal structures were disrupted and an amorphous material was produced by heating at this temperature range (Sujeong et al., 1999). Pozzolanic activity values of samples decreased when this temperature range was exceeded (e.g. when $T > 600–800$ °C). This fall of PA can be attributed to decreasing surface area due to heat treatment. The fall of pozzolanic activity values in the range of 800–1200 °C is the result of both surface area decrease and the decomposition of amorphous structures, and formation of new minerals like mullite.

3.4. Compressive strengths of lime mortars produced from heated clays

Taking into account the pozzolanicity tests, K-244 sample was used as pozzolanic aggregates in the preparation of intervention mortars. Intervention mortars were aged at 23 ± 2 °C in 95 to 100% relative humidity for 3 months. After 3 months, their uniaxial compressive strength values (UCS) were determined by using a Shimadzu AG-I Mechanical Test Instrument.

Compressive strength results (Table 5) showed that the samples containing thermally treated clay (600 °C) gained higher compressive

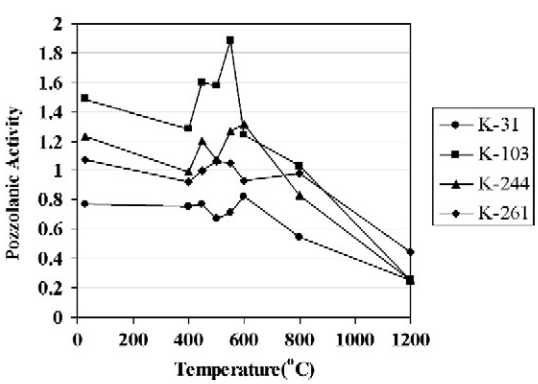

Fig. 7. Pozzolanic activity test results of clay samples heated at temperatures between 200 and 1000 °C.

Table 5
Compressive strength test results of mortar samples prepared by using K-244 clay sample after 3 months of aging.

Mortar no.	Pozzolana	Compressive strengths of the three samples (MPa) (3 months)			Average
1	K244 (unheated)	0.82	0.78	–	0.8
2	K244 (600 °C)	4.46	4.94	5.75	5.05
3	K244 (1000 °C)	1.84	2.43	–	2.14

strength values compared to other clay samples that were either unheated or excessively heated at 1000 °C. This result shows the consistency of the pozzolanicity tests with the compressive strength tests.

4. Conclusions

In this study, mortar samples collected from Manisa Çukur Hamam and Hacet Mescidi were characterized and were found to be hydraulic due to the use of natural pozzolanic aggregates. A series of four different commercial clay samples were selected for study to find out whether they would be applicable as a pozzolanic additive in an intervention mortar after a thermal treatment. The results showed that commercial clays can be used as good pozzolanic aggregates if they are heated between 500 and 700 °C.

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