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Physico-chemical and mineralogical study of ancient mortars used in Harran area (Turkey)

Hanifi Binici[*1], Mehmet Akcan[2], Orhan Aksogan[3] and Rifat Resatoglu[4]

[1]Ceyhan Construction Company, Baskonus Street, Beyza Apt.9, Kahramanmaras, Turkey
[2]Department of Civil Engineering, Kahramnaras Sutcu Imam University, Kahramanmras 46100, Turkey
[3]Toros University, Department of Civil Engineering, Mersin 33140, Turkey
[4]Near East University, Nicosia, North Cyprus

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Abstract. Very limited studies have been accomplished concerning the historical structures around Harran area. Collected mortar samples from the historic structures in the area were tested to explore their mechanical, chemical and mineralogical properties. Mortar samples from three different points of each historical structure were taken and specified in accordance with the related standards taking into consideration their mechanical, chemical and mineralogical properties. By means of SEM-EDX the presence of organic fibres and calcite, quartz, plagioclase and muscovite minerals has been examined. Additionally, by means of XRF analysis, oxide (SiO_2, Al_2O_3, and Fe_2O_3) percentages of mortar ingredients have been specified, also. According to the test results obtained, it was confirmed that the mortars had densities ranging between 1.51-2.10 g/cm^3, porosity values ranging between 8.89-35.38% and compressive strengths ranging between 5.02-5.90 MPa.

Specimen HU, which has the highest durability and lowest water absorption and porosity, was the mortar taken from the most intact building in the mosque complex. This result is most likely due to the very little fine aggregate content of HU. In contrast, HUC mortars with a small amount of fine particles and brick contents yielded slightly lower compressive strengths. The interesting point of this study is the mineralogical analysis results and especially the presence of ettringite in these historic mortars linked to the use of pozzolanic materials. Survival of these historic structures in Harran Area through centuries of use and, also, having been subjected to many earthquakes can probably be explained by these properties of the mortars.

Keywords: harran; mortars; physico-chemical

1. Introduction

As the greatest artifacts of the cultural heritage, historical structures have to be protected and utilized fastidiously. Since mortars, bricks and stones used in those historical structures provide significant information regarding the construction technology of the period of their use, they have a historical documentation value. Historical structures and the materials used in their construction are significant artifacts that should be studied (Oguz *et al.* 2015). Bonding, filler and solidification

*Corresponding author, Ph.D., E-mail: hanifibinici@gmail.com

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materials obtained by mixing water at certain ratios is called "mortar" (Mehta and Monteiro 2005). The mortar and plaster obtained by using lime was used in the constructions of the buildings from ancient Greek, Roman and following periods until the cement was found. Lime mortar and plaster are obtained by mixing lime as binder and fine aggregates as filler materials. It is also known that lime or mortar with organic and inorganic materials are involved in the preparation of lime mortars (Boke 2006). Lime is divided into two types, hydraulic lime and non-hydraulic lime. Non-hydraulic lime is pure form of lime, also called lime or high calcium lime. Advanced analysis shows that the Romans used only non-hydraulic lime. Mortars prepared with non-hydraulic lime hardens when it absorbes CO_2 (Akman *et al.* 1986). The size, the strength, and the content of the mortar and the strength of the plaster are directly influenced by the aggressor. Sand, brick and tile fragments, broken stone, marble and tras were commonly used in historical buildings (Akbulut, 2006). In addition to the type of aggregate, its mineralogy, amount in the mixture and maximum particle size distribution and the ratio of binder to its amount in the mortar affect the performance of the mortar (Stefanidou, and Papayianni 2005). It was noticed that in the second century, pozzolan reacted with lime to produce hydraulic properties. This reaction was made with a mixture of pozzolan and pyrethane which is a volcanic tuff used in Roman style. The Romans knew that lime-pozzolan mixed mortars were better than lime mortars and most frequently preferred to use these mortars. It has also been used in walls, vaults, and even in many civil architectural structures (Moropoulou *et al.* 2005). To achieve this advantageous property hydraulic lime and / or natural pozzolan has been added as binder, in case where the strength and durability of the hydraulic mortars are higher than the other one. Horasan mortar, which is also a type of lime mortar, involves clay products like bricks, tiles, etc. and is also considered to be hydrolic (Oguz *et al*. 2015).

The characterization of hydraulic mortars used in ancient cistern and bathhouses dating back to Byzantine period has been studied in a previous work in which mechanical pyhsico-chemical and micro characteristics of these mortars have been examined. It has been determined that hydrated lime and materials with pozzolanic nature were used as bonding agent in those mortars. While aggregates present in them show different granulometric structures, mostly siliceous and kiln fragments were, also, observed. These structures still stand almost same as in old times despite being used for a long time and under extremely bad interior and exterior conditions mainly due to the fact that their mortars were produced to resist these effects sufficiently (Stefanidou *et al.* 2014, Rizzo *et al.* 2008, Ugurlu and Boke 2009, Boke *et al.* 2006). It has been observed that mortars used in historical structures contain pozzolanic material and crushed brick ballasts. Moreover, it has been found out by means of analyses that dead lime and various aggregates have been used in these mortars (Ozkaya and Boke 2009, Torraca 1982, Degryse *et al.* 2002, Moropoulou *et al.* 2002, Boke and Akkurt 2003).

In general, such mortars have been used in the construction of various structures of Roman, Byzantine, Seljuk and Ottoman periods (Miriell 2011, Gulec and Tulun 1997, Bakolas *et al.* 1998). Turkish, Roman, Byzantine and Medieval mortars have been examined by many authors (Ipekoglu *et al.* 2007, Boke *et al.* 2000, Binici *et al.* 2010, Binici 2016, Cultrone *et al.* 2007, Binici *et al.* 2010, Boynton 1980).

Roman mortars have been highly appreciated for their durability. Hence, their physico-chemical and microstructural characteristics have been widely investigated (Malinowsky 1979). However, the main technological properties of the Ottoman mortars, such as the mechanical strength, durability, and permeability, are not sufficiently well known to enable correlations to be established with their microstructure. The concrete manufacturing process consists of two parts,

Fig. 1 The map of the region

the first of which is the development of macro-porosity of a micro-mortar matrix made of cement, lime, sand and water. The other one is the addition of an expansive agent, which reacts with the water and the lime liberated by the hydration of the binder (Wittman 1983). The gas released during the foregoing chemical reaction causes the fresh mortar to expand and leads to the development of pores, which give the aerated concrete its well-known characteristics, i.e., the low weight and high thermal improvements (Narayanan and Ramamurthy 2000). Moreover, the high porosity of aerated concrete, essential to its main function, which is thermal insulation, leads to very poor mechanical strengths compared to normal concrete. The quantity of pores and the pore distribution mainly influence the mechanical properties (Alexanderson 1979).

In this study, the aim is to specify the mechanical, chemical and mineralogical properties of mortars used in historical structures in Harran Region, namely Şanlıurfa Castle, Harran University, Harran City Walls, Harran Castle and Harran Great Mosque. In addition, it is also aimed to obtain a scientific source to be employed for producing suitable mortars for the restoration practices to be performed within the region.

2. History of Harran

Known history of Harran dates back to around 5000 BC. At first, when the region was under the control of Sumerians and Hittites, the region was invaded by Semites in 2750 BC. The Arabs who have conquered this region in 750 AD, ended the Byzantine dominance. There is a rumor that this is the place called “Haran” in Torah. The name Harran has survived until today without changing for 4000 years. The name Harran, derives from Sumerian and Akkadian “Haranu” which means “Travel-Caravan”. Many world-famous scholars have grown up in Harran University which

Fig. 2 Sanlıurfa Castle and cross-section of the studied mortars

Fig. 3 Harran University and cross-section of the studied mortars

Fig. 4 Harran city walls and cross-section of the studied mortars

is known to have existed since the first age. Sabit bin Kurra who was born in 821 and was a great mathematician, physician and translator of Greek philosophers' works to Arabic and Cabir bin Hayyan who said, contrary to Greek philosophers that the smallest particle of matter could be split with a great energy and would destroy a city such as Baghdad and thus is considered to be the finder of atom. During the reign of the Abbasid caliphate Harun al-Rashid, "Harran University" acquired great fame around the world. Harran which witnessed the settlement of Turkish-Islam states such as Fatimids, Zengids, Ayyubids and Seljuks, was invaded by Mongols at the start of 1260s. When the Mongols realized that they couldn't keep this region, they ruined the city by destroying its Mosque, walls and castle in 1270. Surviving Monuments in Harran are: Harran

Fig. 5 Harran castle and cross-section of the studied mortars

Fig. 6 Harran ulu mosque and cross-section of the studied mortars

Burial Mound-The mound which is located in the center of the city and has a height of 22 m is spread in a fairly large area. Harran Burial Mound which was continually inhabited from III. Millennia BC until XIII century AD contains architectural ruins belonging to various periods and documents which will reveal the region's history. Harran Castle and City Walls-The exact construction date of the elliptical walls surrounding the Old Harran city within the Harran town of Şanlıurfa could not be determined. It is pentagonal and looks as if it is built by a master. Harran Great Mosque-The mosque located at the eastern foothill of Harran Mound is mentioned with the names, Cami el-Firdevs and Cuma Mosque (Friday Mosque) in various sources. Harran Territory map that was used in this study is shown in Fig. 1.

3. Material and method

3.1 Material

Three mortar samples have been taken in accordance with the standards from three different parts of each of the historical structures mentioned before, namely Şanlıurfa Castle, Harran University, Harran City Walls, Harran Castle and Harran Great Mosque. While taking the mortar

Table 1 Visual analysis of mortar samples

Building	Date Built (15)	Sample code	The purpose of the mortar	The type and amount of aggregate in mortar	Sample color
Sanliurfa castle	900	SK	Masonry mortar	It contains river aggregate	
Harran universty	2nd Millennium BC	HU	Rubble Masonry mortar	It contains very little fine aggregate	
Harran city walls	1200	HSS	Brick Masonry mortar	It contains a small amount of fine particles and bricks	
Harran castle	1200	HK	Rubble Masonry mortar	It contains a small amount of fine particles and bricks	
Harran ulumosque	800	HUC	Brick Masonry mortar	It contains a small amount of fine particles and bricks	

samples, special attention was paid not to spoil the unique structures of the mortars and photos were taken of the places from where each sample was taken (Figs. 2-6).

3.2 Method

3.2.1 Visual analyses

In order to obtain prior information about the properties of the mortar samples taken from the historical structures under study, visual analyses of the mortar samples were performed. For this purpose, 4x4x4 cm cubic samples were used. The qualitative observations performed on the mortar samples obtained were accomplished in the following sequence. First of all, the dusts on the surfaces of the mortar samples were extracted by means of a compressor. Mortar samples, with clean surfaces, were examined carefully to determine the organic fiber contents, aggregate types and their ratios within the mortar. Then, the original colors of the mortar samples were determined by means of a color reader (Table 1).

3.2.2 Physical analyses

3.2.2.1 Water absorption rates of the samples by weight and by volume

In order to determine the water absorption rates of the samples water absorption tests were conducted (Teutonico 1988, TS EN 13755 2003, Altun *et al.* 2009). For this study, 4x4x3 cm prismatic samples were used. Three specimens were taken for each group and values that were 10% different from the mean values were discarded. After the surface dusts of the mortar samples had been cleaned via a compressor, the samples were dried in a stove for 48 hours under 60°C temperature. Then, the mortar samples taken out from the stove were cooled in the desiccator and their dry weights were recorded. Then, they were placed in a container full of water and left there for 48 hours and their water-logged and underwater weights were recorded, also.

3.2.2.2 The apparent and real density values of the samples

Due to the amorphous form of the mortar samples, apparent density determination was made by water absorption tests (RILEM 1980, TS EN 1936 2001). For this study, 4×3×3 cm prismatic samples were used. The samples were dried until they reached unchanging weights, and then by using the weights measured in water absorption test and underwater weights, their apparent densities were calculated.

Pycnometer tests were conducted in order to measure the real densities of the mortar samples. A certain amount of ground mortar from each sample was weighed by sieves with 0,063 mm aperture size. Pycnometers was half filled with deionized water. Then, weighed mortar sample was added to the pyknometer and was shaken in order to make a homogeneous liquid- solid mixture. A vacuum pressure of (2.0±0.7) kPa was applied to the pycnometer until all the air bubbles were completely extracted. Then, the pycnometers were almost fully filled with deionized water and left for the solid matter to settle and the water to become clear. Later the pyknometer was carefully filled to the brim with deionized water, closed with a lid and dried with a dry cloth. Then, the pycnometers were weighed and the value was recorded. The pyknometer was emptied and washed, it was filled to the brim with deionized water only, closed with the lid and dried with a dry cloth after which it was weighed and that value was recorded, too.

3.2.2.3 Porosity values of the samples

To be able to calculate porosity, first of all, the compactness of the sample was calculated with the aid of its apparent and real densities (Candeias *et al.* 2004, Kozlu 2010, RILEM TC 167-COM 2005). For this investigation, 3×3×3 cm cubic samples were used. Using the compactness values, the porosity ratios of the materials were determined.

3.2.2.4 Acid loss rate and granulometric analyses of the samples

For this study, 2×2×2 cm cubic samples were used. The mortar samples, after being dried in the stove at 60ºC and cooled in a desiccator, was kept in a 10% HCI solution until the reaction was completed. Aggregates which were filtered from clay and fiber materials with a filter paper and dried were sieved with sieves set consisting of sieves having 8 mm, 4 mm, 2 mm, 1 mm, 500 μ, 250 μ, 125 μ and 63 μ aperture sizes. Before sieving, aggregate samples were weighted. Then, they were sieved through a set of sieves in a descending aperture size order. Thus, the amount of aggregates which passed through each sieve and did not pass through the next were determined. The whole weighting process was made by a precision scale and the results were recorded.

Acid loss analysis is a method that enables the determination of the ratios of ingredients involved in the mortars such as bounding agent, aggregate and clay. When treated with acid, the bounding agent dissolves while silicate aggregates remain solid without being affected by the acid (Ersen and Gulec 2009, Teutonico 1988, Middendorf *et al.* 1999). Because this method will not be enough by itself for mortar samples containing calcareous aggregates, it will be better to make an evaluation with the information obtained from the results of XRD analyses. For the experiment, at first, 150-200 g of mortar is dried at 60ºC until it reaches stable weight and weighed (M1), it was decomposed by dissolving in 10% HCI solution and was filtered through filter paper (F1). Aggregates remaining without dissolving were washed with water and the filtering process was repeated. Afterwards, the aggregates were dried for 24 hours at 60ºC and were weighed (M2). Filter paper was weighed together with clay-sized aggregates that remained on it (F2). The ratio of the parts which reacted to acid and which did not were calculated with the following formulas and was expressed as percentages.

$$M3 = M2 + (F2 - F1),\ A\% = \left(\frac{M3}{M1}\right) X\ 100,\ B\% = 100 - A\%$$

in which M1: dry weight of sample (g), M2: dry weight not reacting to acid (g),
F1: dry weight of filter paper (g), F2: dry weight of filter with thin aggregates (g),
A: percentage not reacting to acid (%), B: percentage reacting to acid (%)

3.2.3 Chemical analyses

XRF analysis was made with a Spectro IQ II model device. With this analysis; Al_2O_3, CaO, Fe_2O_3, Cr_2O_3, MgO, SiO_2, Na_2O, K_2O, P_2O_5, TiO_2, ignition loss (%) was found and their types and ratios were determined. By using these oxide percentages, hydraulic indexes (HI) and cement indexes (CI) of mortar samples were calculated (Jedrzejewska 1981, Middendorf *et al.* 2005).

3.2.4 Mechanical tests

In order to determine the compressive strengths of the mortar samples, larger pieces were cut with 4×4×4 cm sizes using a hacksaw without damaging . The cubic mortar samples were tested in a uniaxial compression strength device and their strength values were recorded.

3.2.5 Microstructure analyses

In case of electron microscope not providing prior information about the sample and results not making sense, a combined analysis technique, EDX is needed. EDX is an analytic technique used for the analysis or chemical characterization of ingredients in the samples (Lanzon and Garcia-Ruiz 2011, Genestar *et al.* 2006). For this purpose, mortar samples were carefully cut into 10×10×10 mm cubes. Small sized mortar samples were examined under microscope and by making EDX readings at bounding, aggregate and bounding-aggregate sections, the chemical properties of these areas were determined (Ugurlu and Boke 2010, Pekmezci 2012).

Thermal analyses were made using TG/DTA model device. Hydraulic properties of the mortars were determined by TG/DTA analysis. As a result of this analysis, by which weight loss against temperature variation is examined, weight losses (%) between 200-600°C and between 600-900°C were determined. Weight loss between 200-600°C, means extraction of chemically bonded water (H_2O); and weight loss between 600-900°C means the extraction of carbon dioxide (CO_2) due to the calcination of carbonated lime. The hydraulic properties of the mortars are appraised by proportioning lost carbon dioxide and water percents (CO_2/H_2O). It is assumed that the foregoing ratio being between 1 and 10 means that the considered mortar shows hydraulic property, and being between 10 and 35 means it doesn't show hydraulic property (Boke 2010).

4. Results and discussion

4.1 Visual analyses

Colors of bonding agent and aggregates, quantities and type of aggregates within mortars abd organic additives in them were determined by qualitative observations (Table 1). The specific colors of mortar samples are pretty close to each other. It can be said that this may be due to the usage of the local clay and aggregates within the mortar samples. In terms of strength, the mortar samples are strong enough that they cannot be crushed by hand.

Among the ingredients of the mortar samples taken from Harran city walls, Harran caste and Harran great mosque, there are brick ballasts as pozzolanic material. The reason of using brick ballasts is to increase the mortar's bindingness. As inorganic additive among the ingredients of the

Table 2 Water absorption, density, porosity and compressive strength

Sample code	Water absorption (by weight, %)	Water absorption (by volume, %)	Apparent density (g/cm³)	Real density (g/cm³)	Porosity (%)	Compressive strength (MPa)
SK	15,04	21,98	1,45	2,23	10,57	5,43
HU	17,12	24,05	1,57	2,31	18,27	5,90
HSS	11,00	15,34	2,49	2,37	8,89	5,37
HK	16,42	22,08	1,41	2,18	15,38	5,32
HUC	23,71	32,39	1,35	2.11	20,05	5,02

mortar samples taken from Harran city walls, Harran caste and Harran great mosque, there is volcanic ash. When looked at visual analysis results of mortar samples, it is seen that the mortar samples containing pozzolanic material have high pressure resistance.

4.2 Physical analyses

4.2.1 Water absorption rates by weight and by volume of the samples

Water absorption rates, by weight and by volume, of the samples are given in Table 2. The average of water absorption rates by weight of the samples vary between 11% and 23.71%. The lowest water absorption rate by weight is for the mortar samples taken from Harran City Walls and the highest for those taken from Harran Great Mosque.

It is seen that the water absorption rates by weight of the mortar samples are close to the values found during the study performed on the Ottoman mortars in Erzurum (Binici *et al.* 2010). The average of the water absorption rates by volume of the samples vary between 15.3% and 32.39%. The mortar samples taken from Harran City Walls have the lowest water absorption rate by volume. The mortar samples taken from Harran Great Mosque have the highest water absorption rate by volume. We can categorize the water absorption rates by volume of mortar samples in three groups. Water absorption rates of SK, HU and HK samples by volume are close to each other and that of HSS sample is lower compared to the other samples. It is also observed that water absorption rate of HUC sample by weight has a higher value compared to the other samples.

4.2.2 The apparent and real densities and porosities of the samples

The apparent densities of the samples are given in Table 2. It is seen that the apparent densities of mortar samples vary between 1.35 and 1.42 g/cm^3. It can also be observed that the average apparent density of the samples taken from Şanlıurfa Castle is the highest and that of the ones taken from Harran Castle is the lowest. Apparent densities of mortar samples may be categorized in two groups within themselves; it is seen that the apparent density values of SK, HU, HSS and HUC samples are quite close to each other. However, that of the HK sample is lower compared to the others. This may be due to its having higher brick ballast and volcanic ash amount as ingredients. It is also seen that the apparent density value obtained in the present study is close to those found in a previous study on historical structures (Degryse *et al.* 2010).

It is seen that the real densities of mortar samples vary between 1.51 and 2.10 g/cm^3. The mortar samples with the highest real density values are those taken from Harran Castle and those with the lowest are the ones taken from Harran City Walls. The real density values of HU and HUC samples are extremely close to each other, but that of HK sample is higher compared to

Table 3 Acid loss analysis results

Sample code	Acid loss (%)
SK	25,75
HU	21,18
HSS	28,36
HK	30,01
HUC	35,91

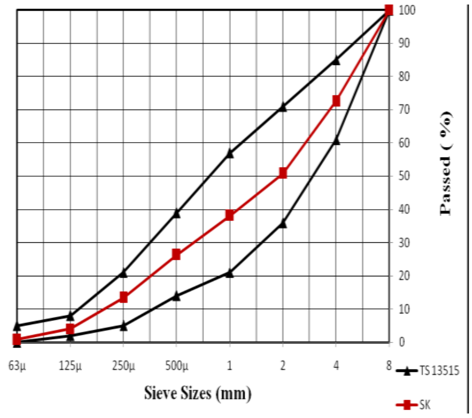

Fig. 7 Aggregate grading curve of SK sample

those of the others.

The real density values obtained in the present study are higher than those found in a similar study conducted on Ottoman mortars in Erzurum (Binici *et al.* 2010). They were lower compared to the real density values found out with a study conducted on Ottoman mortars in Erzurum (Binici *et al.* 2010).

Porosity values of mortar samples vary between 8.89% and 35.38% (Table 2). The sample group with the highest porosity value is the one taken from Harran Castle, while the one with the lowest is the group taken from Harran City Walls. The porosity value of HK sample was found to be higher compared to the others; however, it is not very high compared to those found the study on Ottoman mortars in Erzurum (Binici *et al.* 2010). It should be noted that the porosity values of SK, HU, HSS and HUC match those found in the abovementioned studies.

Porosity value may affect the durability of a mortar against freezing. This is because as porosity increases, more water may penetrate into the mortar and this water causes more cracks to form when it freezes. Since the porosity values of the mortars taken from historical structures within the scope of this study were high, they have shown resistance against the wearing environmental factors. It can also be said that the most relevant factors that keep these structures standing are these properties.

4.2.3 Acid loss of mortar samples

The results of the acid loss analysis are given in Table 3. According to Table 3, the least acid loss was obtained in sample HU while the most acid loss was obtained in sample HUC. These results are in conformity with the other mechanical properties of the mortars.

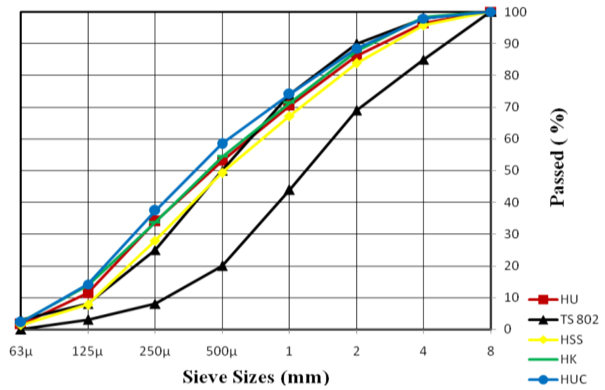

Fig. 8 Aggregate grading curve of HU, HSS, HK and HUCSK samples

Table 4 Element percentages of mortars (by EDX analysis)

Element	Sample code				
	SK	HU	HSS	HK	HUC
Ca	17,90	19,06	25,97	24,20	28,80
Si	13,13	12,34	7,79	5,40	4,73
Al	3,34	3,13	-	2,70	1,22
Fe	4,48	1,32	4,51	1,99	0,64
Mg	2,87	0,97	1,93	1,77	0,97
Total	41,72	36,82	40,20	36,06	36,36
K	4,55	0,75	2,56	1,90	0,93
S	-	11,42	16,00	15,83	12,63
Ti	-	-	0,75	-	0,41
C	8,76	27,48	20,37	10,04	13,66

4.2.4 Aggregate granulometry of mortar samples

It is seen that the particle size distribution (granulometry curve) of the aggregates contained in the ingredients taken from Şanlıurfa Castle is completely within the boundaries of the allowable region defined by EN TS 13515 (Fig. 7). Thus, it can be said that those mortars are in conformance with today's standards. Although not that well, the granulometry curve of the aggregates from Harran Castle is also within the mentioned boundaries (Fig. 8). In the case of Harran City Walls the curve is mostly within those boundaries. On the whole, it can be said that, the conformance with the requirements of the mentioned standard is quite well satisfied, including the Harran University and Harran Great Mosque, also. It is interesting that aggregates used in the mortars of those historical structures which were built hundreds of years ago, are in conformance with today's standards.

4.3 Mechanical tests

Compressive strength of the mortar samples vary between 5.02 and 5.90 MPa (Table 2). The mortar sample with the highest compressive strength is the one taken from Harran City Walls with

Table 5 The oxide concentrations of mortar samples (%) (by XRF analysis)

Component	Sample code				
	SK	HU	HSS	HK	HUC
Na_2O	2,38	0,38	0,66	-	-
K_2O	3,12	1	1,34	1,43	0,87
CaO	60,96	36,89	35,28	37,95	36,23
MgO	1,99	2,1	3,46	2,49	2,24
MnO	0,07	0,03	0,03	0,03	0,04
Fe_2O_3	3	1,8	2,13	2,28	2,13
Al_2O_3	3,62	2,81	3,4	2,83	3,4
SiO_2	16,19	11,13	13,21	10,64	13,09
SO_3	2,34	42,48	38,62	40,63	40,72
P_2O_5	1,00	0,41	0,42	0,38	0,44
SrO	0,08	0,43	0,44	0,45	0,43
TiO_2	0,40	0,23	0,27	0,25	0,29
Total	95,15	99,69	99,26	99,36	99,88
HI	0,36	0,40	0,48	0,39	0,48
CI	0,81	0,89	1,05	0,83	1,06

a value of 5.90 MPa, while the mortar sample with the lowest compressive strength is the one taken from Harran Great Mosque with a value of 5.02 MPa. Thus, it is observed that the compressive strength values of the mortar samples are rather close to each other. A close comparison shows that the compressive strengths of these mortar samples are rather close to the value range of CSIII class mortars stated in EN 988-1 standard. It can then be said that a very important factor allowing these historical structures to survive to the present time is the high compressive strengths of their mortars.

4.4 Microstructure analyses

4.4.1 EDX analysis

The percentages of elements found in the samples with EDX analysis are shown in Table 4. The presence of calcite minerals in the samples indicates the use of lime as binding agent. It is also seen that a large amount of calcium (Ca) element is also contained in the samples. This large amount of calcium element indicates the use of lime during the preparation of these mortars. With EDX analysis, high percentages of calcium, silicium and aluminum elements were also observed. These results indicate that lime and pozzolanic lime react and create hydraulic reaction products, namely calcium-silicate-hydrate (C-S-H) and calcium-aluminate-hydrate(C-A-H). The presence of these minerals must have increased the strengths of the mortars to a great extent.

Among the mortar samples, SK and HU are the ones with the highest ratio of calcium, silicium and aluminum elements. The large amounts of these elements indicate that C-S-H and C-A-H minerals will be denser. At the same time, it is observed that the compressive strengths of these samples are higher than the others. It is observed that the sample with the highest carbon element ratio is HU and the one with the lowest is SK. It can be said that sample HU contains the highest

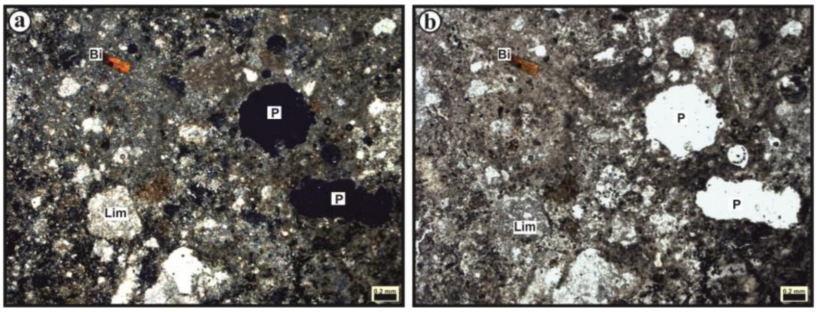

Fig. 9 Photomicrographs in cross-polarized light (a) and plane-polarized light(b) of polished thin sections of Sample SK (Lim: Limestone, P: Pore, Bi:Biotite)

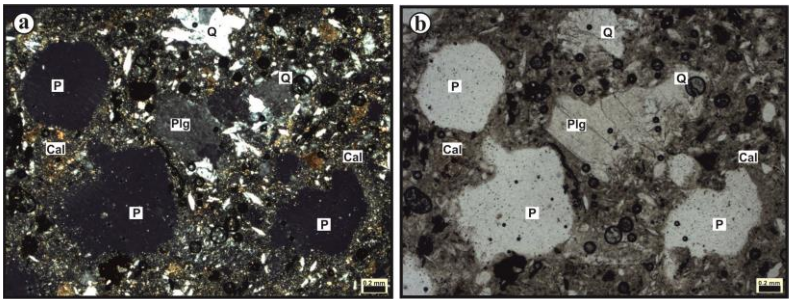

Fig. 10 Photomicrographs in cross-polarized light (a) and planepolarized light (b) of polished thin sections of Sample HU (Cal: Calcite, P: Pore, Plg: Plagioclase, Q: Quartz)

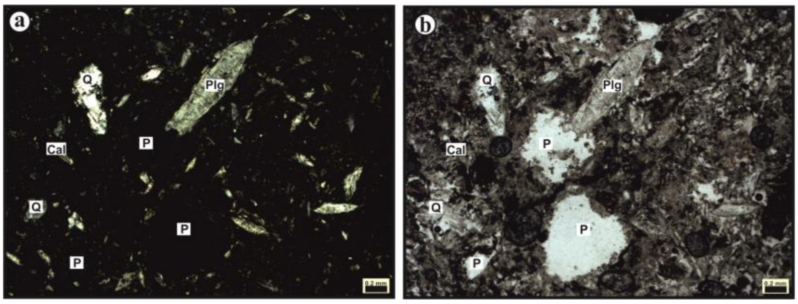

Fig. 11 Photomicro graphs in cross-polarized light (a) and planepolarized light (b) of polished thin sections of Sample HSS (Cal: Calcite, P: Pore, Plg: Plagioclase, Q: Quartz)

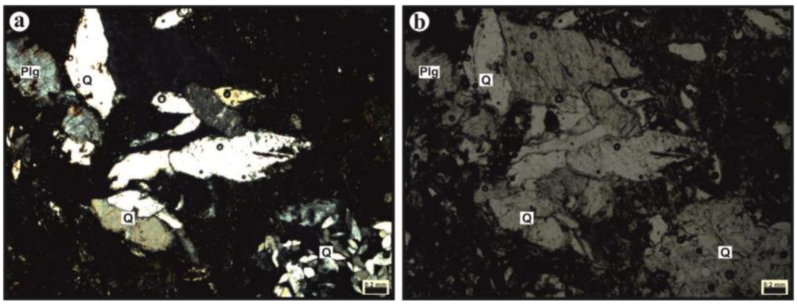

Fig. 12 Photomicro graphs in cross-polarized light (a) and plane polarized light (b) of polished thins ections of Sample HK (Plg: Plagioclase, Q: Quartz)

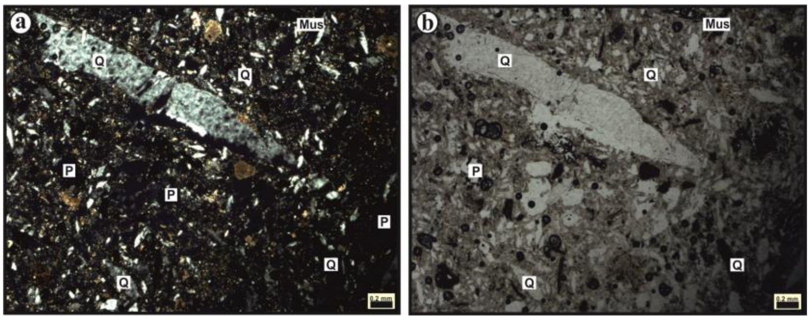

Fig. 13 Photomicro graphs in cross-polarized light (a) and planepolarized light (b) of polished thin sections of Sample HUC (Plg: Plagioclase, Q: Quartz, P: Pore, Mus: Muscovite)

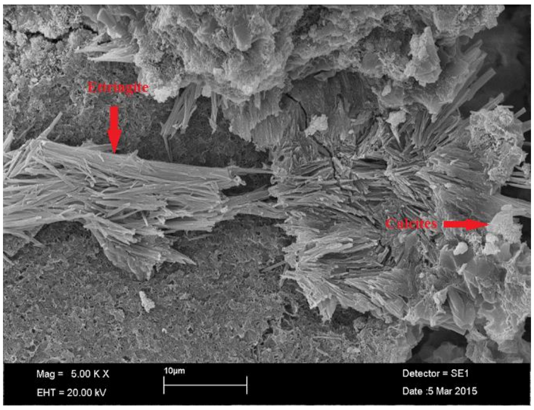

Fig. 14 SEM image of specimen SK

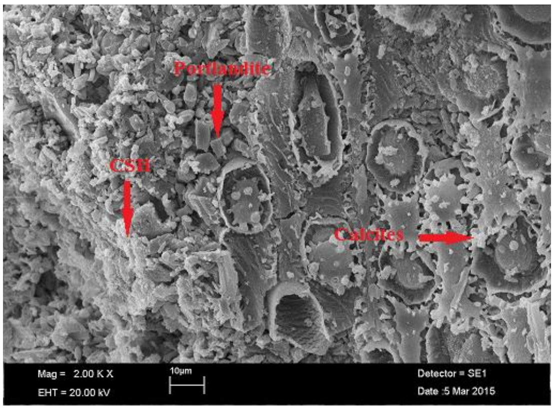

Fig. 15 SEM image of specimen HU

and SK the lowest amount of organic additives.

The presence of Mg and Al elements in the EDX analyses indicate the presence of clay or brick ballast in the mortars. From Table 5, it can be seen that sample SK is the one with the highest Mg and Al element ratios. This shows that sample SK contains more clay or brick ballasts compared to the other samples.

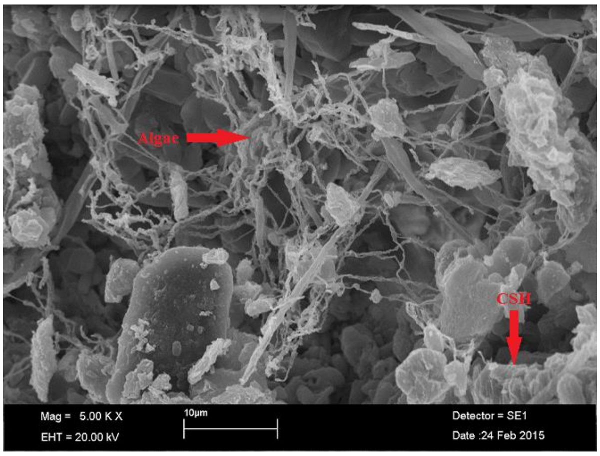

Fig. 16 SEM image of specimen HUC

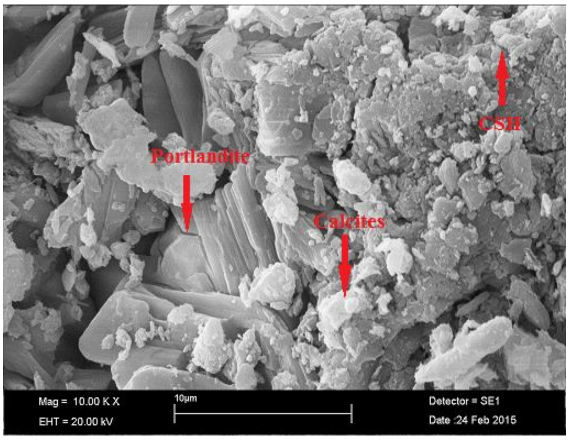

Fig. 17 SEM image of specimen HK

4.4.2 SEM images and thin sections

The characteristics of samples viewed in polarizing microscope are shown in Figs. 9-13. from the photo micrographs in cross-polarized light and plane-polarized light of polished thin sections of samples, it is seen that the microstructure of Harran mortars is very compact and a great deal of limestone, pore, biotite, calcite, plagioclase, quartz and muscovite is also present.

It is observed that HI and CI index values are less than those found in a study conducted on Ottoman mortars (Binici *et al.* 2010). This may be due to the better mechanical and mineralogical properties of Ottoman mortars and their period of usage. It is seen that HI and CI index values of mortar samples HSS and HUC are good. In addition to these index values, CSH, Portlandite, ettringite and calcite minerals are encountered intensely in the SEM images of these samples (Figs. 14-17).

Portlandite mineral improves the strengths of the mortar and the concrete (19). In all the samples, it was observed that minerals were distributed intensely as layers and grains (Fig. 14). Organic fibers are seen clearly in samples HUC and SK (Figs. 15-16). In addition, in all samples, a high degree of binding agent and binding-aggregate interface jamming are observed. Moreover,

Table 6 TG/DTA analysis results

Sample code	H_2O (%)	CO_2 (%)	CO_2/H_2O
SK	14	22	1,57
HU	1	5	5,00
HSS	3	4	1,33
HK	2	3	1,50
HUC	1	4	4,00

Portlandite and ettringite are densely and homogeneously distributed in the samples (Fig. 17). High percentage of Portlandite mineral must have enabled these mortars to preserve their strengths such a long time. The presence of carbon element with SEM/EDX analyses indicates the usage of organic additives (plant-based, animal-based) in mortars in order to enhance the rheology and mechanical properties of the samples.

By performing XRF analysis, the percentages of basic oxides and trace oxides that constitute the structure of the mortars were determined (Table 5).

It is observed that samples contain a high ratio of $CaOSiO_2$ and SO_3. In terms of compound concentrations, it is seen that samples HU, HSS, HK and HUC contain amounts that are close to one another. It is seen that sample SK contains a higher ratio of CaO and a lower ratio of SO_3 compared to the other ones.

It is seen that minerals observed in petrographic analysis (feldspar, ferro magnesium, quartz, and calcite) also support these indexes. Similar to the index values, these samples also have better compressive strength and porosity values. Similar to XRF analysis results, calcite minerals are dominant in mortar matrix and, besides, there are small amounts of silicate, also.

As a result of TG/DTA analyses conducted on samples SK, HU, HSS, HK and HUC, weight losses occurring in specific temperature ranges were also determined. It is observed that the (CO_2/H_2O) ratio (Table 6) of the samples is found to be less than 10, which means that all of the samples have hydraulic property. It is possible to categorize the samples in two groups according to CO_2/H_2O ratios. One group composed of samples HU and HUC have hydraulic properties close to each other. The other group composed of samples SKH, HSS and HUC have close hydraulic properties among themselves and better hydraulic properties compared to the other group. It was also seen that the results of visual, physical, mechanical and microstructure analyses performed on the samples are consistent with each other. Some minerals in the ingredients of the mortars created C-S-H gels. These gels have enhanced the durability properties of mortars. Calcite mineral constitutes the main texture of the mortars. In addition, there are also quartz, Portlandite, ettringite, muscovite, biotite, and plagioclase and ground brick particles. It can be said that the samples which have Portlandite minerals in them, have better binding property. At the same time, it is also observed that the mortars were made with highly porous aggregates.

4.5 General evaluation of mortars from different structures

In this section, all f-mortars are categorized and compared with each other. When structures are thought to have been constructed at very different times, it is expected that the quality of the mortars will be different. However, the oldest HU mortar has a higher compressive strength and a lower mass loss due to acid effect. This is explained by the fine-grained structure of the mortar.

That the youngest mortar, HUC, has the lowest compressive strength and the highest mass loss is explained by the larger grain structure of aggregates in it. The mechanical properties of the mortars obtained from other structures are similar to each other. However, the quality of the mortars of these structures, which were constructed centuries ago by the technology of that day, are not bad at all. Thanks to these mechanical features, they have survived after major earthquakes that have occurred in the region for centuries.

5. Conclusions

1. In the qualitative observations performed on the mortar samples, river aggregate, brick ballasts, clay, volcanic ash and animal hair were observed amongst the ingredients. In the light of these data, it is thought that pozzolanic materials gave strength to the mortars.

2. These values are consistent with the water absorption rates of historical mortars in the literature (Binici *et al.* 2010).

3. Apparent density values of the samples are quite close to one another. The lowest apparent density value belongs to sample HK and the highest to sample SK. However, the apparent density values of all the samples vary in the narrow range 1.35-1.42 g/cm^3. It is understood that the mortars in these structures were made with light materials. As for the real density values of the samples, they vary in the range 1.51-2.10 g/cm^3. It can be said that a certain ingredient content ending up with a high real density value, naturally, has a high strength value as well.

4. The porosity values of the samples varied a lot from each other. Maximum porosity value belongs to HK sample. Volcanic ash is present in the ingredients of this sample as an inorganic additive.

5. It was seen that the aggregate granulometry of the ingredients were within the fine aggregate conformability borders given in TS 13515 or nearly so. Since it is seen that the aggregate granulometry of the ingredients of Harran mortars satisfy the conditions of EN TS 13515, in the restorations of these structures such aggregates which satisfy those conditions can be used.

6. It is seen that the compressive strengths of samples satisfy the requirements of EN 988-1 standard.

7. In the SEM images of the samples, ettringite, CSH and calcite minerals are seen clearly. It can be said that the presence of calcite minerals in SEM images indicates that lime has been used in these mortars as binding agent.

8. It can be said that according to the results of the TGA analyses of the mortar samples they have hydraulic binding properties.

9. Specimen HU, which has the highest durability and lowest water absorption and porosity, was the mortar from the most intact building in the mosque complex. This result is most likely due to its very little fine aggregate content. In contrast, HUC mortars with a small amount of fine particles and brick contents yielded slightly lower compressive strengths.

Depending on the above observations, these structures which have been built in historical Harran region hundreds of years ago and have provided great services do need and deserve to be restored and put under protection before it is too late. They should not be let to disappear. Yet these structures must be handed down to the next generations by performing a simple rehabilitation. Finally, there is no doubt that much more experimental work is required for such a decision. Hence, more works on more specimens should be accomplished, as well as investigations to determine suitable mortars for restoration. The data obtained will shed light on the preservation, restoration and strengthening of these historical buildings in future stages and may be a guide to the people or institutions to conduct research and study on similar historical buildings.

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References

Akbulut, D. (2006), "A proposal for the selection of mortars to be used in the restoration of historical structures", Ph.D. Dissertation, Institute of Science and Technology, Istanbul.

Akman, M.S., Güner, A. and Aksoy, İ.H. (1986), "Horasan history and technique of mortar and concrete features", *Proceedings of the 2nd International Turkish-Islamic Science and Technology History Congress*, Istanbul, Turkey.

Alexanderson, J. (1979), "Relations between structure and mechanical properties of autoclaved aerated concrete", *Cement Concrete Res*., **9**, 507-514.

Altun, F., Tanyeli, G., Kozlu, H. and Dugmeci, O. (2009), *The Properties of Mortar and Plaster Used in the Roman and Byzantine Historic Building*, TUBITAK (Engineering Research Group), Research Project Report, 107M538, Ankara, Turkey.

Bakolas, A., Biscontin, G., Moropoulou, A. and Zendria, E. (1998), "Characterization of structural byzantine mortars by thermogravimetric analysis", *Thermochim Acta*, **321**, 151-160.

Binici, H., Arocena, J., Kapur, S., Aksogan, O. and Kaplan, H. (2010), "Investigation of the physico-chemical and microscopic properties of ottoman mortars from Erzurum (Turkey)", *Constr*. *Build*. *Mater*., **24**, 1995-2002.

Binici, H. and Kapur, S. (2016), "The physical, chemical and microscopic properties of the masonary mortars from Alhambra palace, (Spain) in reference to their earthquake resistance", *Front*. *Architect*. *Res*., **5**, 101-110.

Boke, H. and Akkurt, S. (2003), "Ettringite formation in historic bath brick-lime plasters", *Cement Concrete Res*., **33**, 1457-1464.

Boke, H., Akkurt, S., Ipekoglu, B. and Ugurlu, E. (2006), "Characteristics of bricks used as aggregates in historic brick-lime mortars and plasters", *Cement Concrete Res*., **36**, 1115-1122.

Boke, H., Cizer, O., Ipekoglu, B., Ugurlu, E., Serifaki, K. and Toprak, G. (2000), "Characteristics of lime produced from limestone containing diatoms", *Constr*. *Build*. *Mater*., **22**, 866-874.

Boynton, R.S. (1980), *Chemistry and Technology of Lime and Limestone*, Wiley, New York, U.S.A.

Candeias, A.E., Nogueira, P., Mirao, J., Silva, A.S., Veiga Casa, M., Ribeir, I. and Seruy, A.I. (2004), *Characterization of Ancient Mortars: Present Methodology and Future Perspectives, Chairmen the European Research Councils Chemistry Committees*, Project CATHEDRAL-POCI/HEC/57915/2004.

Cultrone, G., Sebastián, E. and Huertas, M.O. (2007), "Durability of masonry systems: a laboratory study", *Constr*. *Build*. *Mater*., **21**, 40-51.

Degryse, P., Elsen, J. and Waelkens, M. (2002), "Study of ancient mortars from Sagalassos (Turkey) in view of their conservation", *Cement Concrete Res*., **32**, 1457-1463.

Ersen, A. and Gulec, A. (2009), "Simple and advanced analysis methods analysis of the historical funding conservation studies", *KUDEB*., **3**, 65-73.

Genestar, C., Pons, C. and Más, A. "Analytical characterisation of ancient mortars from the archaeological Roman city of Pollentia", *Analy*. *Chim*. *Acta*, **557**, 373-379.

Gulec, A. and Tulun, T. (1997), "Physico-chemical and petrographical studies of old mortars and plasters of

Anatolia", *Cement Concrete Res*., **27**, 227-234.

Ipekoglu, B., Boke, H. and Cizer, O. (2007), "Assessment of material use in relation to climate in historical buildings", *Build. Environ*., **42**, 970-978.

Jedrzejewska, H. (1981), "Ancient mortars as criterion in analysis of old architecture, mortars, cements and grouts used in the conservation of historic buildings symposium", Rome, Italy, November.

Kozlu, H.H. (2010), "Features of characterization of historic mortars and repair mortars in the Kayseri region", Ph.D. Dissertation, Istanbul Technical University, Institute of Science, Istanbul, Turkey.

Lanzon, M. and Garcia-Ruiz, P.A. (2011), "Stabilization of sodium oleate as calcium oleate in cement-based mortars made with limestone fillers", *Constr. Build. Mater*., **25**, 1001-1008.

Malinowsky, R. (1979), "Concretes and mortars in ancient aqueducts", *Concrete Int*., **1**, 66-76.

Mehta, P.K. and Monteiro, P.J.M. (2005), *Concrete: Microstructure, Properties, and Material*, McGraw Hill.

Middendorf, B., Baronio, G., Callebaut, K. and Hughes, J. (1999), "Chemical mineralogical and physical-mechanical investigations of old mortars, historic mortars: Characteristics and tests, international RILEM workshop", Paisley, Scotland, May.

Middendorf, B., Hughes, J.J., Callebaut, A., Baronio, G. and Papayianni, I. (2005), *Investigative Methods for the Characterisation of Historic Mortars-Part 1: Mineralogical Characterization, Materials and Structures*.

Miriello, D., Bloise, A., Crisci, G.M., Apollaro, C. and Marca, A. (2011), "Characterization of archaeological mortars and plasters from kyme (Turkey)", *J. Archaeol. Sci*., **38**, 794-804.

Moropoulou, A., Cakmak, A.S., Biscontin, G., Bakolas, A. and Zendri, E. (2002), "Advanced Byzantine cement based composites resisting earthquake stresses: The crushed bricky lime mortars of justinian's hagia sophia", *Constr. Build. Mater*., **16**, 543-552.

Moropoulou, A., Bakolas, A. and Anagnostopoulou, S. (2005), "Composite materials in ancient structures", *Cement Concrete Compos*., **27**, 295-300.

Narayanan, N. and Ramamurthy, K. (2000), "Structure and properties of aerated concrete: A review", *Cement Concrete Compos*., **22**, 321-329.

Oguz, C., Turker, F. and Kockal, U.N. "Properties of Roman, Byzantine and Seljuk period mortar in andriake harbour", *IMO Tech. J*., **429**, 6993-7013.

Oguz, C., Turker, F. and Kockal, U.N. (2015), "Andriake port of Roman, Byzantine, Seljuk and properties of mortar", *Dig. Mag*., **429**, 6993-7013.

Ozkaya, O. and Boke, H. (2009), "Properties of Roman bricks and mortars used in Serapis temple in the city of Pergamon", *Mater. Charact*., **60**, 995-1000.

Pekmezci, I. (2012), "Cukurova region (cilicia) historical characterization of some mortars used in construction and repair mortar for suggestions", Ph.D. Dissertation, Istanbul Technical University, Institute of Science, Istanbul, Turkey.

RILEM TC 167-COM (2005), "Investigative methods for the characterization of historic mortars-part 2: chemical characterization", *Mater. Struct*., **38**, 387-388.

RILEM (1980), "Tentative recommendations, comission-25-PEM, recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods", *Mater. Constr*., 13/73, 173-253.

Rizzo, G., Ercoli, L., Megna, B. and Parlapiano, M. (2008), "Characterization of mortars from ancient and traditional water supply systems in Sicily", *J. Therm. Analy. Calorim*., **92**, 323-330.

Stefanidou, M. and Papayianni, I. (2005), "The role of aggregates on the structure and properties of lime mortars", *Cement Concrete Compos*., **27**, 914-919.

Stefanidou, M., Pachta, V., Konopissi, S., Karkadelidou, F. and Papayianni, I. (2014), "Analysis and characterization of hydraulic mortars from ancient cisterns and baths in Greece", *Mater. Struct*., **47**, 571-580.

Teutonico, J.M. (1988), *A Laboratory Manual for Architectural Conservators*, ICCROM, Rome.

Teutonico, J.M. (1988), *A Laboratory Manual for Architectural Conservators*, ICCROM, Sintesi Grafica, Rome.

Torraca, G. (1982), *Porous Building Materials*, ICCROM, Rome.

TS EN 13755 (2003), *Turkish Standards, Determination of Water Absorption in the Natural Stones*.

TS EN 1936 (2001), *Natural Stones Test Methods: Real Density, Apparent Density, Total and Open Porosity Determination*, The Turkish Standards Institute, Ankara, Turkey.

Ugurlu, E. and Boke, H. (2010), "Features of lime mortar and plaster and brick to be used in khorasan conservation to be produced", *Proceedings of the 5th National Congress and Exhibition of Building Materials*, Istanbul, Turkey.

Ugurlu, E. and Boke, H. (2009), "The use of brick-plasters and their relevance to climatic conditions of historic bath buildings", *Constr. Build. Mater.*, **23**, 2442-2450.

Wittman, F.H. (1983), *Development in Civil Engineering. Autoclaved Aerated Concrete Moisture and Properties*, Elsevier, the Netherlands.

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