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Physical–Mechanical and Mineralogical Properties of Fired Bricks of the Archaeological Site of Harran, Turkey

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Abstract: In this study, the physical–mechanical and mineralogical properties of bricks used in historical structures of the site of Harran, Turkey have been investigated. Harran was destroyed by the Mongol army, during the Turkish reconquest campaign around the 1260s. The remains of the buildings made of bricks and basalt/limestone were recently uncovered almost in their entirety. Several brick samples have been taken from the burial mound, the university, the city walls, the castle, and the great mosque. From the visual analyses, it was noted that the bricks have unique colors such as pottery, desert beige, and canyon. Physical analyses show that the absorption rates of the bricks are between 17.30–38.12%, their densities between 1.33–1.70 g/cm^3, and porosities between 8.88–25.31%. For the mechanical analyses, the bending strengths have been found to be between 0.82–1.86 MPa and compressive strengths between 6.69–7.95 MPa. The thin-section images show that the bricks contain calcite, muscovite, and plagioclase quartz and pyroxene minerals.

Keywords: brickwork; mechanical testing; cultural heritage conservation; structural analysis

1. Introduction

Conservation, preservation, and restoration of cultural heritage assets and buildings is an emerging topic nowadays. Protection of the heritage created over the thousand-year history of human civilization has become urgent also, considering the increasing numbers of natural and man-made hazards [1–3].

It is a challenging topic and requires a multidisciplinary approach, involving experts of different fields. The implementation of guidelines and procedures was set by the early 20th century, such as *Carta del Restauro* (Athens Charter for the Restoration of Historic Monuments) [4] in 1931, the Venice Charter [5] in 1964, and in ICOMOS (International Council on Monuments and Sites) concerning research, documentation, and technical support regarding cultural assets [6,7]. The final document of the 1974 UNESCO conference [8] and the European Council guidelines [9] regarding the protection of Architectural Heritage represented a keystone in this area. Recently, new methods and procedures have been developed to study historical constructions by means of visual inspection, in-situ testing, non-destructive techniques, photogrammetry, laser scanning, etc., and very promising and satisfactory results have been obtained [10–27].

Turkey is one of the top few countries in the world in terms of great diversity and vast number of heritage monuments/structures [28,29]. Protection of this heritage is enforced by Turkish law, and several conservation institutes and statutory agencies have been established [30]. However, enacting laws and conservation institutes are not always sufficient to protect historical structures. Active studies based on scientific data need to be made along the legal obligations for protection [31].

Identification of the physical and mechanical parameters of constitutive materials of heritage masonry is an important step for their analysis. Previous studies [32–38] conducted on bricks used in historical structures have shown that the density of bricks used in the Ottoman period in an Anatolian fortress built in the 13–14th centuries is 1.66 g/cm^3, their porosity 32.4%, and absorption rate 19.5%. Densities of Ottoman bricks from the 14–15th centuries are determined as 1.7–1.8 g/cm^3 and their porosity rates as 33–37% [32]. Weights per unit volume of 13–14th centuries Byzantine period Yoros Castle bricks are in the range 1.59–1.85 g/cm^3. Their porosity rates are in the range 23–39% and their absorption rates by mass vary in the range 14.4–25.2% [33].

For bricks from the fourth–sixth centuries, from a Serbian archaeological area in Belgrade, the porosity rates of the bricks have been confirmed to be in the range 18.4–19.4% [34]. The bricks of later and longer periods (10–19th centuries) in Toledo, Spain, had water absorption rates in the range 19.0–22.0%, densities in the range 1.60–1.51 g/cm^3, and total porosity rates in the range 32.5–43.1% [35]. It was confirmed with various methods that mineral ingredients of the materials also had effects on various properties of the bricks in addition to firing temperature. The water absorption rates of the Roman bricks from the third–fifth centuries in Toledo were found to be in the range 6.7–12.6%, their weight per unit volume in the range 2.0–1.9 g/cm^3, and porosities in the range 22.2–25.1% [36].

In a study on the mortars and bricks of the Temple of Serapis in Bergama from the Roman–Byzantine period (seventh century), the porosity rates of the bricks have been found in the range 32–35% and their unit weights in the range 1.6–1.7 g/cm^3 [37]. In a study conducted on the bricks of the historical Kutahya Castle, it was found that they had unit weights varying in the range 1.34–1.51 g/cm^3, porosity rates in the range 35.9–45.5%, compressive strengths in the range 9.9–13.7 N/mm^2, and they had pozzolanic natures [38].

A study has been conducted on 43 different batches of clay bricks by the Turkish Ministry of Development and the Housing General Directorate of Construction Materials Laboratory between 1964 and 1975 [26]. In the compressive strength tests conducted in that study, the average compressive strength was found to be 5.39 MPa; the highest value being 10.29 MPa, and the lowest 2.25 MPa. Clay brick samples were taken from brickyards within Ankara's provincial borders in accordance with the standards. In some of the compressive strength tests of historical bricks, an average of 1.57–2.65 MPa compressive strength have been determined for 67 different clay bricks.

In this study, the aim is to specify the physical–mechanical and mineralogical properties of mortars used in historical structures in the Harran region, namely the university, the city walls, the castle and the great mosque. The final aim will be to set up a scientific source for obtaining suitable bricks for restoration applications to be performed within the region in the light of these data.

2. The Site of Harran

Modern Turkey's Harran is a very old outpost of human civilization, and its masonry structures and infrastructure were constructed, repaired, enlarged, or reduced over a very long period of time. The ancient Harran used to be an important city in the Upper Mesopotamia, whose historical records date back to 5000 BC. In the beginning, it was under the control of Sumerians and Hittites, and then, around 2750 BC, the region was conquered by Semites. During the Roman times (first century BC–fifth century AD), Harran, known as Carrhae, was along the border with the Parthian Empire and it was the location of the Battle of Carrhae in 53 BC [39,40], in which the Parthians defeated the Romans under the command of Crassus, who was killed. The city passed under the control of the Eastern Roman Empire (in that period the city was known as Ελληνόπολις or Κάρραι) and, finally, in 750 AD, the Arabs invading the region ended the Byzantine dominance. After the settlement of the Turkish states of Fatimids, Zengids, Ayyubids, and Seljuks [41], the city was conquered by the Mongols around the 1260s. In this long period of time, the city flourished and was a major urban agglomerate in the region. The city and its monuments are cited in a large number of old documents and historic records. When the Mongols were expelled in 1270 by the Turkish army, the city was partially destroyed: the mosque, the city walls, and the castle were highly damaged by the Mongols.

The most important monuments of the city are:

Burial Mound: This monument which has partially survived until today is located in the center of the historic site of Harran, has a height of 22 m, and is spread over a fairly large area. This monument has been continually used from the 3rd century BC until the 13th century AD. The masonry ruins it contains belong to various periods. It is worth noting that several samples of cuneiform scripts were found here, dating its construction to the Sumerian period. According to a hypothesis difficult to prove at the moment, the burial mound should be identified with a moon temple. A moon cult ruled the Plains of Harran for several centuries, before the diffusion of Christianity and Islam. More evidence about this monument could be found in the near future, also considering that the burial mound is actually an active excavation site [42].

Castle: The exact date of construction of this masonry structure is not known. Recently, an ancient Greek inscription was found near the south-east gate: this could help with dating (the Byzantine period of the fourth–seventh century). However, it is likely that, in the ninth century, the Castle, after the conquest of the Arabs (seventh century), was enlarged and restored. According to professor Önal from Harran University [42], this was initially a palace, and it was turned into a castle-like structure with polygonal towers during the turbulent periods of invasions of Mongols and the Crusades (11–13th centuries). In fact, the city of Harran was near the border with the Christian state of the County of Edessa (today Şanlıurfa in Turkey). According to the historic records, the Castle was heavily damaged and almost destroyed during the Mongolian invasions (13th century).

The site is in the process of being added to UNESCO's World Heritage Temporary List [43]. Recently, excavations have been carried out at the castle and nearby buildings with the support of the Turkish Ministry of Culture and Tourism. The excavations carried out on the second floor of the Palace revealed a three-domed bath: the cold, warm, and furnace sections of the bath were completely uncovered. Part of the Castle was recently re-constructed using similar stonework (Figure 1). The archeological site of Harran is not yet fully open to public: according to professor Önal [42] the site was supposed to be accessible at the end of 2019, but the Covid-19 pandemic has likely delayed this.

Figure 1. Harran Castle was partially reconstructed in 2013.

According to the detailed survey by Rice [44], carried out around 1950, the Castle is a three-story building, with tens of rooms. The masonry material is mainly cut stones (basalt and limestone blocks of varying sizes, some of them over a meter long).

City Walls: The exact date of the elliptical walls surrounding Old Harran is not known. Recent excavations (2012–2013) of the Şanlıurfa Museum Directorate, under the consultancy of Professor Mehmet Önal [45], carried out excavation works for restoration purposes on the western part of the city wall, uncovering the city walls, several brickwork towers, and bastions. In excavations in the northern part of the Castle, a gallery was discovered on the west side. It is likely that the construction of the walls dates back to the Roman–Byzantine period: near the south-east gate, an inscription in ancient Greek was found set in a wall. In 2016, excavations were carried out on the city wall (west of the southern, "Raqqa" Gate), revealing part of the wall and leading to the discovery of a broken statue of a woman with a Syriac inscription and a male relief, both used as spolia in the wall. In the 2014–2016 excavations carried out in the west side of the Castle, a crenellated corridor belonging to a second defense system adjacent to the wall of the Castle (between the polygonal and rectangular towers) was uncovered.

Great Mosque: The great mosque is considered the oldest mosque built in Anatolia as part of the Islamic architecture. This mosque is known as the Paradise Mosque. It is a stone and brickwork masonry construction, built by the last Ummayad caliph Mervan II in 744–750. The plan of the building has the dimensions of 104 × 107 m. The mosque was recently unearthed during the excavations led by Dr Nurettin Yardimer [45]. These excavations are currently being carried out also outside the northern and western gates. Only small portions of the mosque remain standing today: the 33.3 m tall minaret, the fountain, the mihrab, and the eastern wall. The masonry members have gone through several restoration processes. The mosque, which is located at the eastern foothill of the burial mound, is also known by the names Cami el-Firdevs and Cuma Camisi (Friday Mosque).

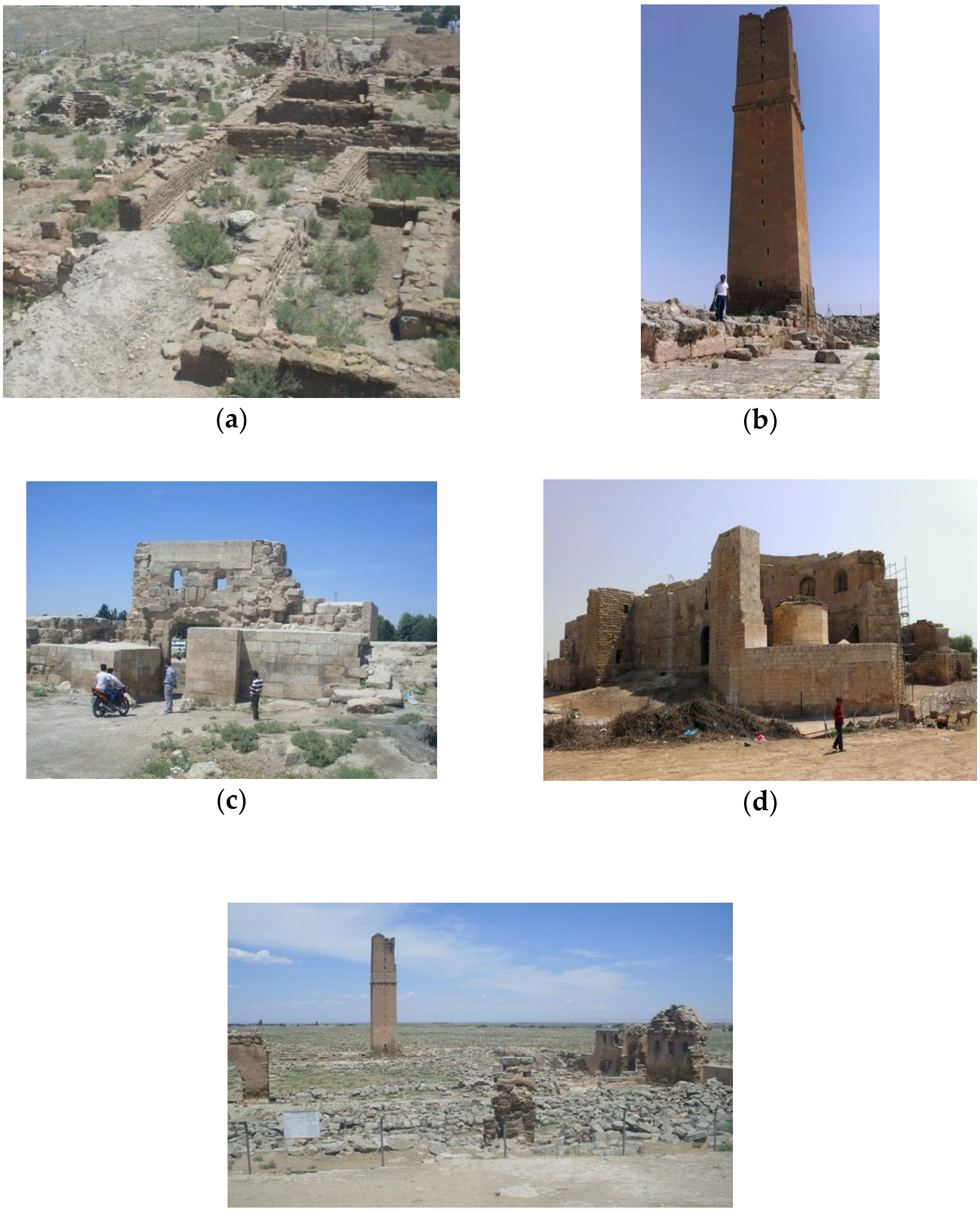
A historic copper map of the region is given in Figure 2. It can be noted that the site of Harran, 44 km southeast of Şanlıurfa, is located in a strategic region near the historic and modern border with Mesopotamia, Syria, and Persia, under the Southeastern Anatolia mountain range.

Figure 2. The map of the studied region in a historic copper engraving from the 18th century.

3. Materials and Methods

3.1. Materials

Five brick samples were taken from different historical ruins of the city: the burial mound, the university, the city walls, the castle and the great mosque, from undisturbed parts of these buildings. While extracting the brick samples, special attention was paid not to spoil the unique structures of the bricks and photos of places from where the samples were taken, and photos of the taken brick samples were filed. The five selected buildings are shown in Figure 3. A detail of a wall of the burial mound is given in Figure 4.



(**a**) (**b**) (**c**) (**d**) (**e**)

Figure 3. Iconic monuments in the historic city of Harran: (**a**) burial mound, (**b**) university, (**c**) city walls, (**d**) castle, (**e**) great mosque.

Figure 4. Brick sample taken from the burial mound (HBM).

3.2. Methods

Brick samples were used for testing purposes. In detail, samples were subjected to visual analysis, water absorption and weight density measurements, bending and compressive testing, and mineralogical analysis. Table 1 shows the test matrix. The reader should be alerted to the limited experimental data base (also considering that the test results lack the statistical properties) from which these analyses started.

Table 1. Test matrix.

Location of Sample	Sample Designation	Visual Analysis	Water Absorption	Wei ghtDensity	Bending Strength	Compr. Strength	Mineral. Analysis
Burial Mound	HBM	√	√	√	√	√	√
University	HU	√	√	√	√	√	√
City Walls	HCW	√	√	√	√	√	√
Castle	HC	√	√	√	√	√	√
Great Mosque	HGM	√	√	√	√	√	√

3.2.1. Visual Analyses

In order to obtain prior information about the properties of the brick samples taken from the historical structures, visual analysis of the brick samples was performed. Initially, inconsistent material on the surfaces of the brick samples was removed by means of an air compressor. After cleaning their surfaces, brick samples were examined thoroughly. It is common to find natural fibers embedded into the structure of solid bricks from this period and region. However, this was not the case in the bricks extracted in Harran: there were no natural fibers (organic additive) present in the tested samples (Table 1). In order to determine the original colors of the brick samples, which surface dusts, the colors of the brick samples were determined using a colorimeter (model X-Rite RM200), and the color codes found out were specified by the corresponding colors on the color chart.

3.2.2. Physical Analyses

The test for water absorption is generally a good indication of the freeze/thaw resistance, and it provides important information about the durability of bricks. Water absorption is measured by how much a brick increases in weight after it has been soaked in water. In order to determine the water absorption rates of the bricks used at Harran, a series of laboratory tests were conducted [46]. Initially inconsistent material, traces of organic and inorganic materials (lime mortar, mold, etc.) had been removed from the brick samples via an air compressor. Subsequently, the brick samples were dried in an oven for 48 h at 60 °C and cooled in a desiccator. The samples were dried until the weight gain remained unchanged. At the end of this procedure, the samples' dry weights were recorded. Then, brick specimens were soaked for 48 hours in water, after which their water-logged and underwater weights were recorded.

The aim of this investigation was also to calculate the density of the bricks used at the site of Harran. It is well-known that density is an elementary physical property, and, for a homogeneous object, it is defined as the ratio of its mass (m) to its volume (V). However, due to the amorphous form of the brick samples, apparent density was initially calculated using the results of the water absorption tests [47,48], by considering the volume and weights of the brick specimens, in their dry and water-impregnated states.

However, pycnometer tests were also conducted in order to measure the real densities of the brick samples [49]. Furthermore, to calculate the porosity values of the brick samples, compactness was calculated from the test results in terms of the apparent and the real densities [50].

3.2.3. Mechanical and Mineralogical Analyses

Samples were prepared by reducing the bricks to the dimensions of 40 × 40 × 160 mm with a hacksaw. Prepared samples were placed on the testing machine on one of the lateral surfaces upon the support cylinders in such a way that the longitudinal axis would be normal to the support cylinders (Figure 5). The load was applied normal to the lateral surface of the prism via the loader cylinder, with its axis normal to the longitudinal axis of the specimen, and the load was increased gradually at the rate of (50 ± 10) N/s until the sample was broken [51].

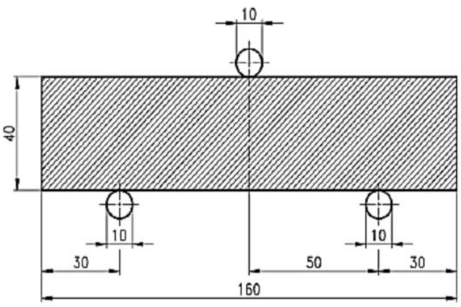


Figure 5. Bending test arrangement (units in mm).

The compressive strengths of the brick samples were determined by measuring the uniaxial compressive strength, applying the compressive load on the prismatic samples obtained from the broken halves of the bending strength test specimens [52]. The bending strength (s$_{bend}$) was initially calculated using:

$$\sigma_{bend} = \frac{3F_{sd}L_0}{2bd^2}, \quad (1)$$

where F_{sd} is the maximum bending load, L_0 is the bending span (100 mm), b and d are the width and height of the brick specimen (40 mm).

And the compressive strength (s$_{compr}$):

$$\sigma_{compr} = \frac{F_{sc}}{bd}, \quad (2)$$

where F_{sc} is the maximum compressive load.

In this analysis, which helps the determination of the texture and minerals of brick samples, at first the samples in bulk, which would represent the petrographic properties of the material, were dried for 2 h under 105 ± 5 °C after the dusts on them had been brushed away. The dried samples were first let to absorb epoxy polymer under pressure and let to dry. Then, they were cut in thin sections in a section-preparation device and were glued with epoxy polymer. After the necessary cutting and thinning processes in the thin-section device, they were polished. The texture of the sample, bounding aggregate ratios, bounding aggregate phases, aggregate types, shapes and sizes in the prepared polished sections were determined via a stereo microscope (single nicol). Later, these sections went through thinning and polishing processes so that they could be examined under the polarizing microscope. Working on the section prepared by thinning until the thickness of 30 μ was reached, the definite identification of minerals, decomposition, newly created minerals and the textural properties formed by them were examined by using the polarizing microscope (two nicols) [53].

4. Results and Discussion

4.1. Visual Analyses

The colors of bonding agent and aggregates, quantity and type of aggregates within brick, and, if present, organic additives within brick ingredients were determined by qualitative observations (Table 2).

Table 2. Visual analyses of the brick samples.

Sample Designation	Colour of Sample	Used in	Organic Additives
HBM		Walls	No
HU		Partition walls	No
HCW		Partition walls	No
HC		Partition walls	No
HGM		Partitions of the mosque	No

The specific colors of the brick samples are close to those of the clays contained therein. In terms of strength, the brick samples are strong enough such that they cannot be broken by hand. The shapes of the brick samples are rectangular and square. Rectangular and square shapes enable easier and regular building of walls.

4.2. Physical Analyses

Physical analyses allowed us to determine the water absorption rates by weight and by volume of the brick samples. Apart from the compressive strength, it is well-known that water absorption is an important property in brickwork masonry. This property can affect the quality of the brick itself and the bond strength between the brick and mortar in masonry structures and can result in reducing its strength properties. The authors [25] have previously conducted an experimental investigation to assess the physical, mineralogical, and chemical properties of the lime mortars used in the monuments of Harran. The test results carried out on the lime mortar and on the units (i.e., the bricks) could be critical for any future conservation measure and assessment of the structural safety of the masonry structures of the site of Harran: this could highly facilitate the estimation of the mechanical properties of the brickwork masonry. Water absorption rates by weight and by volume of the samples are given in Table 3. Figure 6 shows the tested specimen during soaking in water.

Table 3. Water absorption rates by weight and by volume of the samples.

Sample Designation	Water Absorption by Weight (%)	Water Absorption by Volume (%)
HBM	32.35	41.16
HU	25.46	33.35
HCW	17.30	26.64
HC	18.49	25.54
HGM	38.12	45.43

Figure 6. Water absorption tests.

The water absorption rates of the brick samples by weight vary between 17.30% and 38.12%. The lowest water absorption rate by weight was obtained from brick samples taken from the city walls. The highest water absorption rate by weight was obtained from brick samples taken from the great mosque. The water absorption rates by volume of the brick samples vary between 25.54% and 45.43%. Brick samples taken from the castle have the lowest water absorption rate by volume. A mortar sample taken from the great mosque has the highest water absorption rate by volume. When the water absorption rates of the brick samples are evaluated in accordance with Turkish Standard 704 [54], it is seen that the water absorption rates are high. The reason for this might be the method or the ingredients used during their production.

Furthermore, the volumes of the brick samples have been determined via water absorption test since they were not prismatic in shape. Then, apparent densities of the brick samples have been compiled (Table 4).

Table 4. The apparent and real densities and porosity values of the brick samples.

Sample Designation	Apparent Density (g/cm^3)	Real Density (g/cm^3)	Porosity (%)
HBM	1.27	1.70	25.31
HU	1.31	1.46	10.28
HCW	1.54	1.69	8.88
HC	1.38	1.58	12.65
HGM	1.19	1.33	10.53

The real densities of the brick samples vary between 1.33–1.70 g/cm^3. The brick sample with the highest real density value is the one taken from the burial mound. The brick sample with the lowest real density value is the one taken from the great mosque. Real density values of the brick samples are within the range specified by Turkish Standard 704 (1.20–2.00 g/cm^3) [54]. Real densities of the brick samples falling within the range specified in the Turkish Standard indicates that a serious controlled production procedure has been used for making them.

Porosity values of the brick samples were calculated using their apparent densities and real densities. During the firing of the bricks, infinite microscopic cracks, cavities, and gaps are formed (pores) [55]. These pores are, especially, effective in the failures of the bricks. In general, when the porosity of a brick goes above 25%, its compressive strength gradually decreases. One of the most significant factors which affected the durability of the brick samples is their porosity. Since harmful liquids easily penetrate into the bricks with higher porosity values, their durability decreases. The porosity values of the brick samples vary between 8.88% and 25.31%. The brick sample with the highest porosity value is the one taken from the burial mound. The sample with the lowest porosity value is the one taken from the city walls. Since porosity value affects the strength and durability of a brick, the porosity must be kept below a particular value so that a desired brick quality is guaranteed. As the porosity values of the bricks studied in this research are low, that must be the reason why these historical structures have survived to date.

Compressive strength tests on the fired brick samples were carried out to determine the load-carrying capacity of bricks, together with analysis of the lime mortar [25] to estimate the compressive strength of the brickwork masonry. Because Turkey is one of the most active seismic regions in Europe and Asia (Figure 7), it was decided to measure the bending strength of the bricks. This mechanical property could be useful for an estimation of the tensile and shear strengths of the brickwork masonry used at the monuments of Harran, this providing interesting information about the seismic vulnerability of Harran buildings. Unfortunately, given the high level of protection by the Turkish authority over the site of Harran, it was not possible to conduct more exhaustive or full-scale testing on the brickwork masonry. The bending and compressive strengths of the brick samples are given in Table 5.

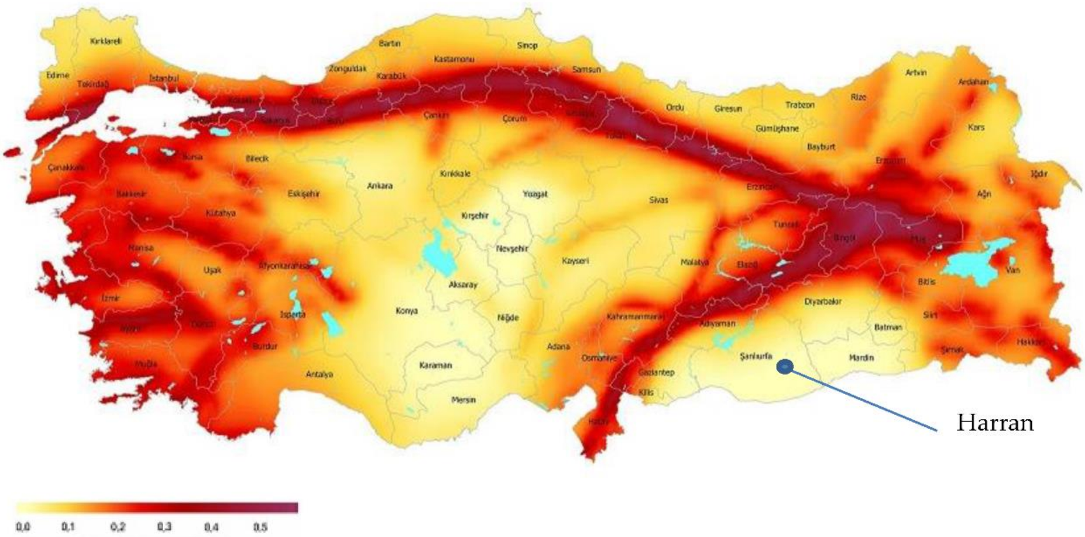


Figure 7. Seismic risk map of Turkey [56], in terms of the ratio between peak ground acceleration a_g and g (g = acceleration of gravity), for a probability of exceedance of 10% in 50 years (475 years return period).

Table 5. The bending and compressive strengths of the brick samples.

Sample Designation	Bending Strength σ_{bend} (MPa)	Compressive Strength σ_{compr} (MPa)
HBM	1.86	7.95
HU	1.36	7.18
HCW	1.24	6.69
HC	1.26	7.43
HGM	0.82	7.21

A large amount of information is available about the geology of the region of Harran. This is located in the basin of the Balikh river. This joins the Euphrates at the modern city of Raqqa. Figure 8 shows a geology map of the area of Harran: it can be noted that the rocks of the valley belong to the

Quaternary period, being the most recently laid geologic strata. Based on the low seismic risk of the area of Harran and its geology, with likely a low local amplification over a rocky soil, we can conclude that the seismic hazard for the site of Harran is relatively low. However, the site deserves a more in-depth analysis, also considering hazards from climate change (heavy rain falls, flooding, etc.) and their combined effects on the masonry monuments of Harran.

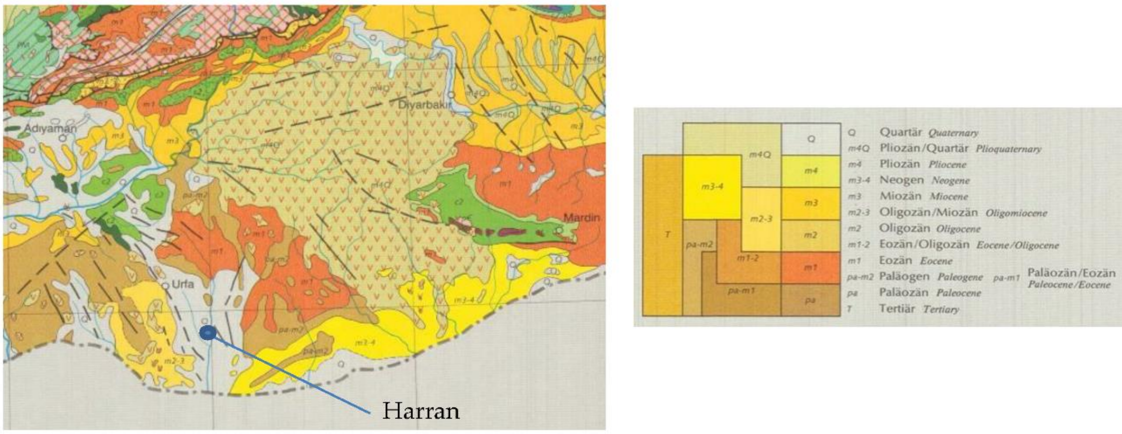


Figure 8. Geology of the area of Harran.

Figure 9 shows several brick specimens before these were reduced to the standard testing dimensions. This figure also shows the testing instrument used for both bending and compression tests. The bending strengths σ_{bend} of the brick samples vary between 0.82 and 1.86 MPa. The brick sample with the highest bending strength is the one taken from the burial mound. The brick sample with the lowest bending strength is the one taken from the great mosque.

Figure 9. Specimen preparation and instrumentation used for bending and compression tests.

The compressive strengths σ_{compr} of the brick samples vary between 6.69 and 7.95 MPa. The brick sample with the highest compressive strength value is the one taken from the burial mound. Figure 10 shows a brick specimen before being subjected to the compressive load: the underlying brick debris from previous tests clearly demonstrate that the samples' failure mode was due to crumbling/pulverization of the tile material. This is a well-known failure mechanism that is normal for low-strength, porous masonry materials [57].

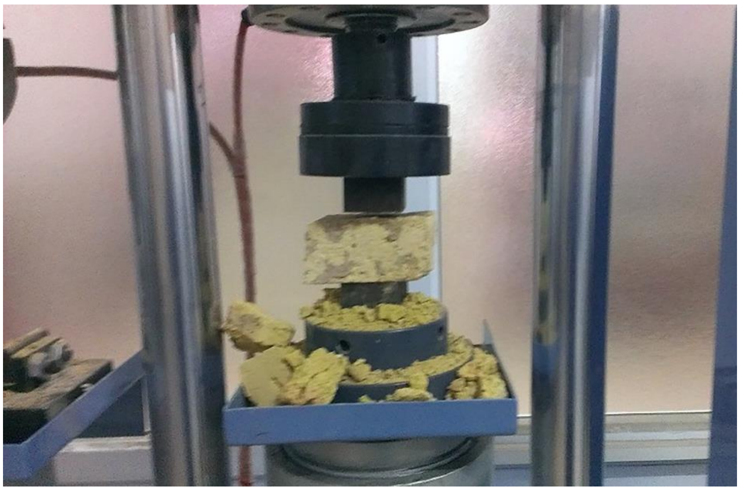


Figure 10. Compression test: the crumbling failure mode of brick specimens subjected to a compressive loading can be noted. This was the consequence of the low compressive strength and porosity.

The sample with the lowest compressive strength value is the one taken from the city walls. According to previous studies [58], it is possible to say that the compressive strength values of the brick samples are very similar and in a limited range (6.69–7.95 MPa). This could suggest that the Harran monuments, constructed in different periods of time, have been manufactured using a similar or non-time-varying technology, labor, resources, and environmental conditions. This could strengthen the hypothesis that local skills, construction materials, and methods were passed down from father to son for generations in family brick companies, also considering the frequent changing of rulers (from Parthians to Romans, from Byzantines to Arabs, and finally to the Mongols and Turkish). The thin-section images of the five brick samples taken from the historical structures are quite similar to each other (Figure 11).

Figure 11. Detail of the brick cross-section.

In order to scan the minerals and the pores in the brick samples more clearly, single- and two-Nicol prism filters were used to capture the images. There is an excessive amount of calcite mineral in the HBM brick sample. Also, it can be noted that it contains muscovite, plagioclase, and oxide minerals. These minerals are bonded with calcite (Figure 12). Excessive amounts of calcite mineral are also present in the HU brick sample. It was also concluded that it has a porous structure, containing, in addition to calcite minerals, plagioclase and quartz minerals. Plenty of quartz and calcite minerals are present in the HCW brick sample, consisting of tiny grains.

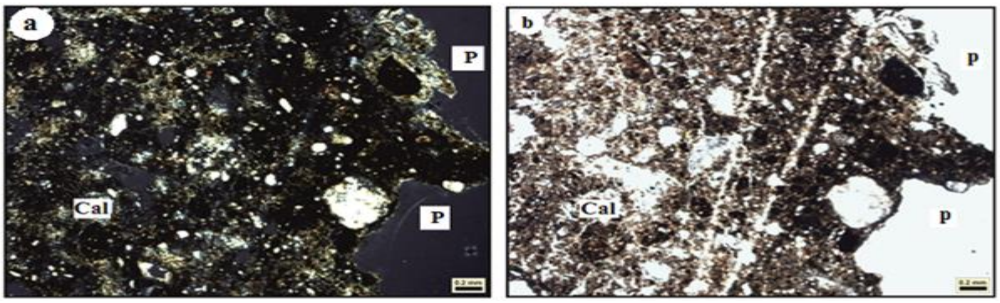


Figure 12. Photo micro graphs of polished thin sections of the HH brick sample, (**a**) in cross-polarized light and (**b**) in plane-polarized light (P: Pore, Cal: Calcite).

It could be interesting to compare the brick mechanical properties of the Harran monuments with the ones of other sites in the region. Because most of these sites are listed and protected it is very rare to find these values in the scientific literature, given the destructive character of these tests. Table 6 shows these data for a limited number of sites located in Greece and Turkey. It can be noted that the compressive strengths of Harran bricks are consistent with the mechanical characteristics of the Serapis temple of Pergamon (second century), in Bergama, Turkey, and with the ones of Ottoman Ördekli Bath, Bursa, Turkey, but smaller compared to the compressive strengths of some Roman and Byzantine masonry monuments located in Filippi, Greece.

Table 6. Comparison of test results on bricks of other sites in Asia Minor, Southern Europe, and Northern Africa.

Site	Compressive Strength σ_{compr} (MPa)	Density (g/cm^3)	Porosity (%)
Serapis temple, Pergamon, 2nd century, Bergama, Turkey [59]	6.0	1.65	35
Agia Sophia, Istanbul, Turkey, 6th century [60]	-	1.55–1.90	45
Ottoman Ördekli Bath, Bursa, Turkey, 14th century [61]	8.9–10.1	1.70	38-39.8
Filippi, Greece, 2nd century [62]	18.78	1.678	22.02
Galerius Palace, Greece, 4th century [62]	19.80	1.756	15.78
Site of Dion, Greece, 4th century [62]	4.62	1.638	22.38
Site of Palatiano, Greece, 4th century [62]	20.72	1.69	15.96
Byzantine monuments, Thessaloniki, Greece, 7–11th century [62]	4.5–16.08	1.46–1.84	16.02–29.8
Roman Babylon of Egypt, 4th century, [63]	1.6–9.2	1.4–1.8	17.3–43.2

On the other hand, the density of Harran bricks seems significantly smaller compared to the density of bricks used in Turkey in historic brickwork constructions. For example, the porosity of the bricks of the Serapis temple, Pergamon; Agia Sophia, Istanbul; and Ottoman Ördekli Bath, Bursa, are 35, 45, and 39%, respectively (Table 5). Harran bricks exhibited a porosity ranging between 8.88 and 25.31 %, with a mean value of about 13% (Table 4).

By comparing the mechanical properties of the bricks and the mortar used in Harran with other archeological monuments in the macro-Mediterranean region, critical information can be obtained. For example, conservation interventions successfully implemented in other sites, based on their property similarity with the masonry materials, can be adopted with more confidence. Conservation of archeological monuments requires a deep knowledge of structures and constituent materials, of their properties, context features and use conditions, and of the possible state of damage and its causes. Prevention and rehabilitation measures can be successfully accomplished only if a proper analysis and diagnosis has been formulated, so that masonry heritage buildings can be preserved as much as possible as historic documents of our past.

For the Harran site, several questions remain without answers: this relates to the sites from where the inhabitants of Harran collected the raw materials used for brick production, the technologies they applied to make and fire the bricks. It could be very interesting to study how far they transported raw resources and final products after furnace treatments, considering that a crucial point was the nearby availability of timber, water, and sandy soils without stones. This paper aims to provide a limited, but significant contribution to these critical issues.

5. Conclusions

In this paper the physical–mechanical and mineralogical properties of bricks used in historical masonry structures of the ancient city of Harran were investigated. At the end of the study, the following conclusions can be drawn:

1. The visual analyses of the bricks allowed to describe them based on their colors. Importantly, this is a potential source of cultural and heritage information and can provide useful information about the identity, chronology, technology, labor, resources, and environmental conditions of the site of Harran, in Turkey.
2. The mechanical properties (compressive and bending strengths), porosity, and density of the bricks have been compared with the scarce existing data for other sites in the macro-region (Asia minor, southern Europe, northern Africa). Also taking into account the limited experimental base, it can be concluded that the mechanical properties are consistent with the ones of other sites, even if a large scattering of results was noted from one site to another. It seems that bricks' mechanical characteristics from Roman times for sites in Greece are higher (18–20 MPa for the compressive strength) compared with the compressive strength of the buildings constructed in the Late Antiquity (3rd–10th century).
3. It is also possible to note that the compressive and bending strength values of the tested brick samples are very similar and in a limited range (6.69–7.95 MPa for compressive strength, and 0.82–1.86 MPa for bending strength). This could suggest that the Harran masonry monuments, constructed in different periods of time, have been manufactured using a similar or a non-time-varying technology, labor, resources, and environmental conditions. This could strengthen the hypothesis that local skills, construction materials, and methods were passed down from father to son for generations in the family brick companies and were not shattered by the destructions and devastation from frequent wars, changing of rulers, natural disasters that affected the area of Harran.
4. The mechanical characterization of the masonry constituent materials (bricks and mortar) of several Harran monuments represents a critical information for future analyses regarding the seismic vulnerability, and the implementation of conservation interventions.
5. The minerals seen in the thin-section images of the bricks are cryptocrystals, quartz, ferro magnesium, calcite, and opaque minerals. It can be said that the ferro magnesium minerals within the bricks provide a binding material support to the bricks by decomposition.

These structures in Harran Area, which were built centuries ago (since 5000 BC), provided great services. These structures are extremely valuable as cultural heritage. Thus, before it is too late, they need to be restored and put under protection. With planned restorations on these structures, by taking into consideration the scientific studies conducted on them, being our cultural heritage, they must be handed on to the coming generations.

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References

1. Mustafaraj, E. *Assessment of Historical Structures, A Case Study of Five Ottoman Mosques in Albania*; LAP Lambert Academic Publishing: Saarbrucken, Germany, 2014.
2. Borri, A.; Corradi, M. Architectural heritage: A discussion on conservation and safety. *Heritage* **2019**, *2*, 41. [CrossRef]
3. Yardım, Y.; Mustafaraj, E. Selected Assessment and Retrofitting Application Techniques for Historical Unreinforced Masonry Buildings. In *Handbook of Research on Seismic Assessment and Rehabilitation of Historic Structures*; Asteris, P.G., Plevris, V., Eds.; IGI Global: Hershey, PA, USA, 2015; pp. 525–545.
4. Lorusso, S.; Carbonara, G.; Gentile, M.T. Architectural restoration: different conceptions during centuries. *Conserv. Sci. Cult. Herit.* **2002**, *2*, 56–83.
5. Venice Charter. *International Charter for the Conservation and Restoration of Monuments and Sites*; ICOMOS Archnet-IJAR: Venice, Italy, 1964; Volume 12, pp. 334–346.
6. Elia, R.J. ICOMOS adopts archaeological heritage charter: text and commentary. *J. Field Archaeol.* **1993**, *20*, 97–104. [CrossRef]
7. ICOMOS–ISCARSAH Committee. ICOMOS Charter—Principles for the analysis, conservation and structural restoration of architectural heritage. In Proceedings of the ICOMOS 14th General Assembly and Scientific Symposium, Victoria Falls, Zimbabwe, 27–31 October 2003.
8. The General Conference of the United Nations Educational, Scientific and Cultural Organization meeting in Paris from 17 October to 21 November 1972, at its seventeenth session. In Proceedings of the Convention for the Protection of the Architectural Heritage of Europe, Granada, Spain, 3 October 1985.
9. Akoz, F.; Yuzer, N. Investigation of Material Properties of Ayasofya Mosque- Sts Sergius and Bacchus-in Istanbul by Using Non-destructive Methods. In Proceedings of the Conference STREMA 95, Structural Studies Repairs and Maintenance of Historical Buildings, Crete, Greece, 4 May 1995; pp. 163–170.
10. Borri, A.; Corradi, M.; Castori, G.; De Maria, A. A method for the analysis and classification of historic masonry. *Bull. Earthq. Eng.* **2015**, *13*, 2647–2665. [CrossRef]
11. Mustafaraj, E.; Yardım, Y. Repair and Strengthening of Historical Structures: Naziresha's Mosque in Elbasan. In Proceedings of the 3rd Annual International Conference on Civil Engineering, Athens, Greece, 10–13 June 2013.
12. Soyluk, A.; Ilerisoy, Z.Y. Dynamic analysis of Dolmabahce masonry clock tower. *Gradevinar* **2013**, *65*, 345–352.
13. Betti, M.; Galano, L. Seismic analysis of historic masonry buildings: The Vicarius Palace in Pescia (Italy). *Buildings* **2012**, *2*, 63–82. [CrossRef]
14. Lourenço, P.B. Assessment, diagnosis and strengthening of Outerio church, Portugal. *Constr. Build. Mater.* **2005**, *19*, 634–645. [CrossRef]
15. Faella, C.; Martinelli, E.; Nigro, E.; Paciello, S. Tuff masonry walls strengthened with a new kind of C-FRP sheet: Experimental tests and analysis. In Proceedings of the 13th World Conference on Earthquake Engineering, Vancouver, BC, Canada, 1–6 August 2004.
16. Yardım, Y.; Mustafaraj, E. Effects of soil settlement and deformed geometry on a historical structure. *Nat. Hazards Earth Syst. Sci.* **2013**, *1*, 5911–5934. [CrossRef]
17. Anzoni, A.; Binda, L.; Carpinteri, A.; Invarnizzi, S.; Lacidogna, G. A multilevel approach for the damage assessment of historic masonry towers. *J. Cult. Herit.* **2009**, *11*, 459–470. [CrossRef]
18. Van Aarle, M.; Schellen, H.; van Schijndel, J. Hygro thermal simulation to predict the risk of frost damage in masonry; effects of climate change. *Energy Procedia* **2015**, *78*, 2536–2541. [CrossRef]
19. Franzoni, E. State-of-the-art on methods for reducing rising damp in masonry. *J. Cult. Herit.* **2018**, *31*, S3–S9. [CrossRef]
20. Franzoni, E.; Gentilini, C.; Graziani, G.; Bandini, S. Mechanical properties of fired-clay brick masonry models in moist and dry conditions. *Key Eng. Mater.* **2014**, *624*, 307–312.
21. Amde, A.M.; Martin, J.V.; Colville, J. The effects of moisture on compressive strength and modulus of brick masonry. In Proceedings of the 13th International Brick and Block Masonry Conference, Amsterdam, The Netherlands, 4–7 July 2004; p. 15043442.
22. Graubohm, M.; Brameshuber, W. Rehabilitation of Masonry constructions temporarily submerged by Water-influence of Water on the properties of Masonry and Facings, Drying Methods and their Effect. In Proceedings of the 11th Canadian Masonry Symposium, Toronto, ON, Canada, 31 May–3 June 2009.

23. Smith, B.M. *Moisture Problems in Historic Masonry Walls: Diagnosis and Treatment*; U.S. Government Printing Office: Washington, DC, USA, 1984.
24. Borri, A.; Castori, G.; Corradi, M. Determination of shear strength of masonry panels through different tests. *Int. J. Archit. Herit.* **2015**, *9*, 913–927. [CrossRef]
25. Uranjek, M.; Bosiljkov, B.V. Influence of freeze–thaw cycles on mechanical properties of historical brick masonry. *Constr. Build. Mater.* **2015**, *84*, 416–428. [CrossRef]
26. Binici, H.; Akcan, M.; Aksogan, O.; Resatoglu, R. Physico-chemical and mineralogical study of ancient mortars used in Harran area (Turkey). *Adv. Concr. Constr.* **2017**, *5*, 639–658.
27. Somuncu, M.; Yiğit, T. World heritage sites in Turkey: Current status and problems of conservation and management. *CBD* **2010**, *8*, 1–26.
28. Corradi, M.; Borri, A. A database of the structural behavior of masonry in shear. *Bull. Earthq. Eng.* **2018**, *16*, 3905–3930. [CrossRef]
29. Ertan, T.; Egercioglu, Y. The impact of UNESCO world heritage list on historic urban city centers and its place in urban regeneration: the case of Melaka, Malaysia and Tire, Turkey. *Procedia-Soc. Behav. Sci.* **2016**, *216*, 591–602. [CrossRef]
30. Bonini, B.S.; Shoup, D.; Zan, L. Understanding cultural heritage in Turkey: institutional context and organisational issues. *Int. J. Herit. Stud.* **2013**, *19*, 728–748. [CrossRef]
31. Garrecht, H. Climatic Problems at Speyer Cathedral-Monitoring as a Contribution to Preservation, RILEM TC 177-MDT. In Proceedings of the Workshop on On-Site Control and Non-Destructive Evaluation of Masonry Structures, Mantova, Italy, 12–14 November 2001.
32. Kurugol, S.; Gulec, A. Physical and Mechanical Properties of Anadolu Hisarı's Mortars. In Proceedings of the ISSM 08, 8th International Seminar on Structural Masonry, Istanbul, Turkey, 5–7 November 2008; pp. 513–521.
33. Boke, H.; Akkurt, S.; Ipekoglu, B.; Ugurlu, E. Characteristics of brick used as aggregate in historic brick-lime mortars and plasters. *Cem. Concr. Res.* **2006**, *36*, 1115–1122. [CrossRef]
34. Radivojevic, A. Investigation of late antique bricks from archaeological sites of contemporary Serbia as a basis of conservation works. *Archit. Civ. Eng.* **2005**, *3*, 185–193. [CrossRef]
35. Lopez-Arce, P.; Garcia-Guinea, J.; Garcia, M.; Obis, J. Bricks in historical buildings of Toledo City: characterization and restoration. *Mater. Charact.* **2003**, *50*, 59–68. [CrossRef]
36. Lopez-Arce, P.; Garcia-Guinea, J. Weathering traces in ancient bricks from historic buildings. *Build. Environ.* **2005**, *40*, 929–941. [CrossRef]
37. Ozkaya, A.O. Properties of Roman Bricks and Mortars Used in Serapis Temple in Bergama. Master's Thesis, Graduate School of Engineering and Sciences of Izmir Institute of Technology, Izmir, Turkey, 2005.
38. Akoz, F.; Yuzer, N.; Cakır, O.; Kabay, N. Investigation of Material Properties of Dolmabahce Palace Reception (Muayede) Hall's Dome and Vaults. *Stud. Anc. Struct.* **2001**, *1*, 659–668.
39. Sampson, G. *Defeat of Rome in the East: Crassus, the Parthians, and the Disastrous Battle of Carrhae, 53 BC*; Pen & Sword Military: Barnsley, UK, 2008.
40. Gray, E.W.; Sherwin-White, S.M.; van der Spek, R.J. *Carrhae*; Oxford Research Encyclopedia of Classics: Oxford, UK, 2015.
41. Freely, J. *A History of Ottoman Architecture*; WIT Press: Southampton, UK, 2011.
42. Daily Sabah. Available online: https://www.dailysabah.com/history/2018/12/26/magnificent-harran-palace-revealed-through-excavations (accessed on 10 July 2020).
43. Turkey's Harran Eyes UNESCO Heritage List. Available online: https://www.aa.com.tr/en/culture-and-art/turkeys-harran-eyes-unesco-heritage-list/1212521#:~{}:text=SANLIURFA%2C%20Turkey,UNESCO\T1\textquoterights%20tentative%20list%20since%202000 (accessed on 10 July 2020).
44. Rice, D.S. Medieval Harran: Studies on its Topography and Monuments, I. *Anatol. Stud.* **1952**, *2*, 36–84. [CrossRef]
45. Turkish Archaeonews. Available online: https://turkisharchaeonews.net/site/harran (accessed on 10 July 2020).
46. Teutonico, J.M. *A Laboratory Manual for Architectural Conservators*; ICCROM: Rome, Italy, 1988; pp. 113–118.
47. RILEM. Tentative recommendations, comission-25-PEM, Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods. *Mater. Struct.* **1980**, *13*, 173–253.

48. TS EN 1936. *Natural Stones Test. Methods: Real Density, Apparent Density, Total and Open Porosity Determination*; The Turkish Standards Institute: Ankara, Turkey, 2001.
49. Candeias, A.E.; Nogueira, P.; Mirao, J.; Silva, A.S.; Veiga Casa, M.; Ribeir, I.; Seruy, A.I. *Characterization of Ancient Mortars: Present Methodology and Future Perspectives*; (Project CATHEDRAL—POCI/HEC/57915/2004); Chairmen the European Research Councils Chemistry Committees: Brussels, Belgium, 2004.
50. Kozlu, H.H. Features of Characterization of Historic Mortars and Repair Mortars in the Kayseri Region. Ph.D. Thesis, Istanbul Technical University, Institute of Science, Istanbul, Turkey, 2010.
51. TS EN 196-1. *Cement Strength Tests*; Section 1; Turkish Standards Institute: Ankara, Turkey, 2002.
52. Ugurlu, E.; Boke, H. Features of lime mortar and plaster and brick to be used in Khorasan Conservation to be produced. In Proceedings of the 5th National Congress and Exhibition of Building Materials, Istanbul, Turkey, 3–5 November 2020; 2010; Volume 3, pp. 385–396.
53. Pekmezci, I. Cukurova Region (Cilicia) Historical Characterization of Some Mortars Used in Construction and Repair Mortar for Suggestions. Ph.D. Thesis, Istanbul Technical University, Institute of Science, Istanbul, Turkey, 2012.
54. TS 704. *Clay Bricks (Wall Tile)*; Turkish Standards Institution: Ankara, Turkey, 1979.
55. Binici, H.; Arocena, J.; Kapur, S.; Aksogan, O.; Kaplan, H. Microstructure of red brick dust and ground basaltic pumice blended cement mortars exposed to magnesium sulphate solutions. *Can. Civ. Eng. J.* **2009**, *36*, 1784–1793. [CrossRef]
56. Turkey Earthquake Risk Map. Available online: https://deprem.afad.gov.tr/deprem-tehlike-haritasi?lang=en (accessed on 10 July 2020).
57. Vasanelli, E.; Colangiuli, D.; Calia, A.; Sbartai, Z.M.; Breysse, D. Combining non-invasive techniques for reliable prediction of soft stone strength in historic masonries. *Constr. Build. Mater.* **2017**, *146*, 744–754. [CrossRef]
58. Binici, H.; Arocena, J.; Kapur, S.; Aksogan, O.; Kaplan, H. Investigation of the physico-chemical and microscopic properties of Ottoman mortars from Erzurum (Turkey). *Constr. Build. Mater.* **2010**, *24*, 1995–2002. [CrossRef]
59. Ozkaya, O.A.; Boke, H. Properties of Roman bricks and mortars used in Serapis temple in the city of Pergamon. *Mater. Charact.* **2009**, *60*, 995–1000. [CrossRef]
60. Moropoulou, A.; Cakmak, A.; Polikreti, K. Provenance and technology investigation of Agia Sophia bricks, Istanbul, Turkey. *J. Am. Ceram. Soc.* **2002**, *85*, 366–372. [CrossRef]
61. Bağbancı, M.B.; Özcan, R.; Bağbancı, Ö.K. Characterization of Materials Used in the Fourteenth Century the early Ottoman Ördekli Bath, Bursa, Turkey. *Stud. Conserv.* **2010**, *55*, 301–312. [CrossRef]
62. Stefanidou, M.; Papayianni, I.; Pachta, V. Analysis and characterization of Roman and Byzantine fired bricks from Greece. *Mater. Struct.* **2015**, *48*, 2251–2260. [CrossRef]
63. Hemeda, S.; Akarish, I.M.; El-Nagga, A.A. Engineering investigations and durability problems of the construction materials of the Roman Babylon of Egypt. *Open J. Geol.* **2018**, *8*, 404–436. [CrossRef]