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Material analysis for restoration application: a case study of the world's first university Mor Yakup Church in Nusaybin, Mardin

Lale Karataş[1], Aydın Alptekin[2*] and Murat Yakar[3]

Abstract

The Mor Yakup Church, located in the Nusaybin District of Mardin, is known as the world's first educational university in history and represents one of the oldest Christian medieval monuments. In this study, it is aimed to determine the factors of the strength problems of the structure by investigating the characterization of building materials and what kind of factors affect the material behavior with various observational and experimental methods. It was determined that the main deterioration types in the materials of the building were erosion, fractures, loss of parts and the dissolve of the joint mortars between the masonry work on the facades. Since the materials used in the construction of the building are unable in terms of physico-mechanics, it has been determined that the severe continental climate conditions prevailing in the region easily cause such physical deterioration on the construction materials. In addition, the presence of clays in the conventional mortar used in the building has been defined as an internal problem that causes the material to get tired with the osmotic pressure it creates by absorbing water. A very high rate of salinization was detected in the building materials of the building and it was observed that this salting was caused by the acid effect caused by air pollution and the portland cement used in the previous repairs in the building. Finally, this study presents restoration recommendations to repair the material deterioration in the building and to prevent its occurrence in the future.

Keywords Limestone, Travertine, Mortar, Decay, Salt crystallization, Acid attack, Structural–textural properties, Index–strength properties

Introduction

The strength of historical buildings depends on the long-term behavior of the materials used in their construction [1]. Experimental analyzes of historical buildings allow characterizing material properties and making predictions about the long-term behavior of materials [2]. Although there are various recommendations for how materials behave in the long term, there is still no universally agreed methodology. Because each material exhibits different behaviors as a result of the interaction of its own internal properties with various external environmental factors. At this point, it is stated in various studies that the results of observational and experimental analyzes should be interpreted on a local/geographical basis and considering the factors which the material interacts [3, 4].

There are studies conducted in different countries of the world that reveal various results related to the durability problems of historical buildings by examining the interaction of the internal properties of the material with external factors. Dettmering and Dai [5] explained that the main content of the materials in the Great Wall of China was lime binder and most of the damage was

*Correspondence:
Aydın Alptekin
aydinalptekin@mersin.edu.tr
[1] Department of Architecture and Urban Planning, Mardin Artuklu University, Mardin, Turkey
[2] Department of Geological Engineering, Mersin University, Mersin, Turkey
[3] Department of Geomatics Engineering, Mersin University, Mersin, Turkey

related to reactions between lime mortars and environmental air pollutants. Fahmy et al. [6] presented results explaining the negative impact of interactions with the geoenvironmental conditions of the Sahure pyramid in Egypt, with the intrinsic defects of the mineralogical content of the building materials, and on the structural stability of the pyramid. Torney et al. [7] concluded that the past use of largely incompatible, impermeable and/or highly cementitious materials as mortars in Scotland was the cause of many problems with moisture retention. Sammartino et al. [8] noted that the damage seen in the oldest section of the church "San Maurizio" in Italy was mainly related to water seeping from the roof and the inability to drain rainwater effectively due to a previous poor restoration. Germinario et al. [9] combined microclimate monitoring methods and experimental analysis of Taya Caves in Japan, and concluded that salt decomposition is strongly related to the physico-chemical properties of waters. Barnoos et al. [10] explained that the structural and chemical properties of the limestone in the Anahita Temple in Kangavar, Iran, were formed due to climatic factors and especially temperature fluctuations. Avşar and Güleç [11] stated that the stones used in the approximately 1500 historical tombstones found in the Seljuk Meydan Cemetery in the Ahlat district of Bitlis province contain weak minerals and particles prone to argillization, and they explained that the majority of the damages are caused by the internal defects of the material.

When the literature on Mardin Province of Turkey is examined, it is seen that there are studies that explain the damage problems of the structures in this region based on the results of experimental analysis. The results of the study on the Mardin Train Station Building showed that the sulfate salts detected in the stones were caused by the acidic effects caused by air pollution, and the chlorine salts were caused by the cement used for repair purposes in almost every part of the building [12]. Experimental results of the properties of the natural stone produced in the quarries of Mardin Yalım village reveal that the stone is resistant to hot climates and frost (up to − 40 °C) and that the climatic conditions of this region cannot affect the strength of this stone in such a way as to cause extensive damage [13]. In the study, which is about the destruction of Mardin Castle, it is explained that the stratification of water-soluble salt caused by air pollution in the humid environment formed in the pores of the stone in the rainy winter season, and efflorescence type deteriorations are observed on the stone surface [14].

Nusaybin district in Turkey's Mardin Province is an archaeological site of prime importance. It is considered one of the richest archaeological sites in Nusaybin. One of the structures in this ruin is the Mor Yakup Church, which is defined as the first university in the world [15]. The building, which has survived through repairs and changes in various periods and partially preserved its architectural integrity, has damages due to various effects and the building is in need of maintenance and repair. When the relevant literature is examined, although there are researches on building materials in Mardin, there is no study related material characterization and the causes of material problems of Nusaybin ruins. In this direction, this study is an important study in terms of determining the characterization and durability problems of the building materials of the Mor Yakup Church located in the ruins of Nusaybin. The main objectives of this article are: (1) characterization of Mor Yakup Church building materials and revealing durability problems; (2) To reveal the objectives to be considered while determining the repair materials in the restoration process of the church. In order to achieve all these goals, in this study, the properties and strength problems of the materials will be determined by using different analytical and experimental techniques for the building materials of the church. The documentation, analysis, laboratory results used in this research will also provide resources for restoration practices of other similar monuments in the vicinity.

Study area

The Mor Yakup Church, located in the Nusaybin District of Mardin Province, represents one of the most important and oldest Christian Medieval monuments that have survived in the region. Built by the Bishop of Nusaybin, Mar Yakup, in 311 AD, the Church has a three-nave basilica (Fig. 1). While it was a pagan structure, it was converted into a church and school in 326 AD. The fact that the building was converted into a baptistery in 359 in the Early Christian period and then into a church in the eighth century makes the building important and different in terms of Christian

Fig. 1 Ruins thought to belong to Mor Yakup Church and Mor Yakup Cathedral

architectural history. The building, whose history is based on pre-Christianity and defined as a "special structure", is evaluated as a baptistery structure connected to the cathedral and monastery complex with the spread of Christianity in the region, and today it is referred to as the Mor Yakup Church and the building is associated with the Syriac Orthodox church [15].

Nusaybin, the district where the building was built, was known as a center of science and culture before Christ. The poet philosopher Vifa who lived long before Jesus and II. Philosopher Mor Ibn Serabyon, who lived in the middle of the century, was one of the Paganist Assyrians who were educated in Nusaybin schools. The first Christian-Assyrian Academy was opened in Nusaybin under the name of Nisibis Academy by Mor Yakup from Nusaybin, one of the founders of the Antakya Academy, in 200 AD. Nusaybin historically known as Nisibis or Nesbin, is a district in Mardin Province, Turkey. The city of Nisibis is one of the oldest settlements in Mesopotamia. The fact that it was established on the meeting point of historical trade routes has carried the city forward in science and economy. Especially the closure of the Edessa School has turned it into an important education center. The church was once the world's first educational center where philosophy, logic, literature, geometry, astronomy, medicine, and law were taught. Important finds in terms of Syriac history were also obtained during the excavations. The oldest inscriptions shed light on Syriac history. It is also important in terms of Syriac literature. Writers and poets such as Mor Efrem were trained. These saints wrote the hymns and texts that are read in churches today [16].

Excavations in the Mor Yakup Monastery, which was once the world's first educational university where philosophy, logic, literature, geometry, astronomy, medicine and law were taught, are still continuing. The fact that the oldest Syriac inscriptions were found here as a result of the excavations strengthens the argument of the Nysibis school as the oldest university. Serious inscriptions are emerging that the Nisibis Academy, which was found in the archaeological excavations in the Mor Yakup Monastery in Mardin Nusaybin, was the first university in the world. Important finds were also obtained in terms of Syriac history.

The inscriptions unearthed here shed light on Syriac history. It is also important for Syriac literature. Writers and poets such as Mor Efrem were trained. These saints wrote the hymns and texts that are read in churches today. As a result of the excavations, a cathedral dated to the fourth century was found in the northwest of the building, and there are building remains designed for different uses in the east and south directions. The building, known as the church, is referred to as the first university of education in the world, which has survived to the present day [17].

The building reflects the characteristics of the Late Roman–Early Byzantine period with its architecture and high relief stone decorations. The building, which has reached today with the repairs and changes it has undergone in various periods and partially preserved its architectural integrity, is still in need of maintenance and repair. After the excavations carried out in recent years, sections of different qualities have emerged in terms of materials, construction techniques and architectural elements on the northern, southern and eastern facades of the building. The southern part of the building is divided into two separate parts by two opposing buttresses. To the east, there is a square-planned space with a width and length of 7 m [18]. (Fig. 2).

There are two door openings on the north and south walls of the place. An apse is visible on the eastern wall. There is an arch opening to the second section in the west. The most important feature of this place is the wall decorate. There are door openings on the north and south walls of the western space. When the position of the buttresses in between and their relationship with other architectural elements are evaluated, it is understood that they were added later. When the eastern wall is examined from the outside, it is seen that the apse part may have been added later. The decorations inside the space are considered to be a deeper and earlier example of the ornamentation that was common in Northern Mesopotamia in the fiveth–sixth centuries and is dated to the fourth century [18] (Fig. 3).

Method

First, the building was examined on site and the material problems of the building were determined observationally. In the next stage, the sample locations were determined. It is allowed to take a certain number of samples from the building. In this context, the opinions of many experts were taken in order to select the most accurate regions that would benefit from revealing the properties and problems of the material related to the building. Laboratory analyzes were carried out by taking 3 mortar, 3 plaster and 2 stone samples (Table 1) from the Mor Yakup Church. Samples taken from the Mor Yakup Church were analyzed in Mardin Museum Restoration-Conservation and Analysis Laboratory, Ankara University Earth Sciences Application and Research Center (YEBİM) and Ankara University Başkent Materials Research Center. Strength properties of the samples (unit volume weight, water absorption capacity, porosity, Schmidt hammer hardness and ultrasonic velocity measurement tests) with physical tests, general texture and mineral content of the

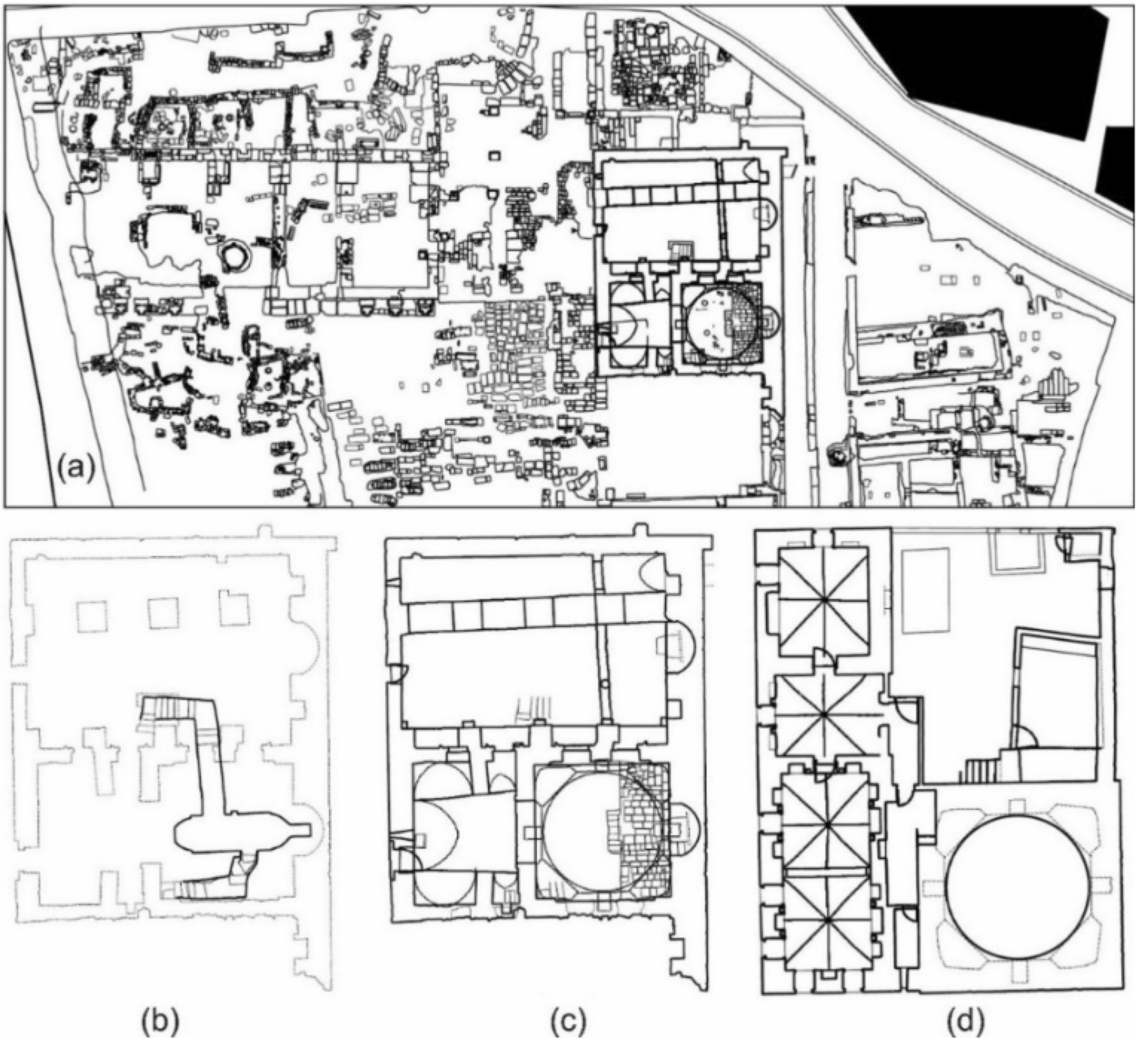

Fig. 2 Measured drawings of the Mor Yakup Church. **a** Plan of measured drawing of Church, **b** − 4.00 level plan of church, **c** 0.00 level plan of church, **d** + 7.50 level plan of church [18]

materials (stereo microscope analysis) with petrographic analysis, moisture organic and carbonate (CO_3^{2-}) content with calcination analysis, water-soluble salts were determined by spot tests and compressive strengths of original mortars were determined by point loading test method (Fig. 4).

Visual analysis and sampling

In this step, on-site visits and field studies were conducted to identify the specific problems of the different construction materials of the building, to gather information about the construction materials and to understand the environmental factors. The samples taken from the building were determined to confirm the environmental effects on the properties of the building materials. During and after the samples were taken, their current status was visually evaluated, described in detail, and documented with photographs (Table 1).

Petrographic analysis

The sections examined by petrological analysis were prepared from samples obtained by immersing dispersed mortar samples in epoxy resin (Araldite AY103—hardener HY956, Ciba-Geigy) [19]. Minerals were defined to qualitatively and semi-quantitatively assess the mineralogical grade of samples. Analysis of these thin sections determined whether there were similarities or differences between the samples with respect to mineral content. Petrological analysis can also help identify acid-soluble particles. After soaking the samples in epoxy, the samples were cut with a low speed saw to obtain thin sections. Sample sections were thinned to 30 microns. Qualitative and semi-quantitative analyzes of minerals were

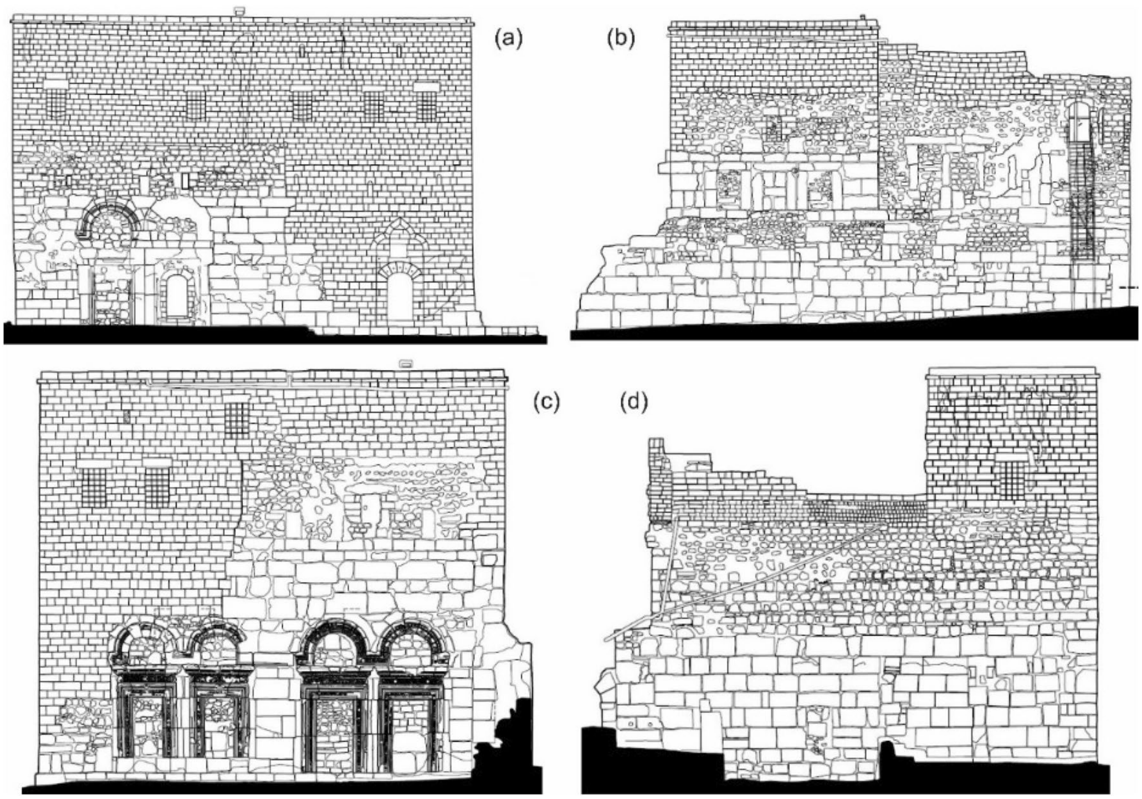

Fig. 3 Facades measured drawings of Mor Yakup Church **a** west façade measured drawings of building, **b** east façade measured drawings of building, **c** south façade measured drawings of building, **d** north facade measured drawings of building

performed under a polarized light microscope. A Leica MZ6 stereo microscope was used for petrological characterization of the samples and the texture and aggregate/binding properties of thin/thick sectioned samples prepared for thin section light microscopy analysis were examined under a stereomicroscope.

Physical analysis

Experiments were performed for saturated unit weight (g/cm^3), dry unit weight (g/cm^3), water absorption capacity (%), porosity (%), Schmidt hammer hardness, and ultrasonic velocity (km/s), and physical determined the characteristics of mortar. After drying at 105 °C, the samples were weighed and saturated with water to determine the natural weight, dry weight and saturated weight. Physical tests were measured and calculated according to TS 699 [20] and ASTM C97 [21]. A stone's moisture content (MC) is expressed as a percentage by subtracting the stone's dry weight from its natural weight and dividing by the dry weight according to the formula MC = (wet weight − dry weight)/dry weight * 100 weight [22]. In addition, the water absorption (WA) is expressed as the weight change rate due to water absorption, and is calculated as WA = (Mwet − Mdry) ÷ Mdry × 100%. The stone density (D) also indicates the unit weight of the stone and is calculated by dividing the mass by the total stone volume using the formula D = m/v [23]. Furthermore, the unit weight (UW) is calculated by the gravitational force acting on the mass and is given by the formula UW = m * g. where the weight is g * mm/s^2. Also, specific gravity (SG) is the ratio of the density of stone to the density of water. Natural stone has a specific gravity of 2 to 3, and is expressed as SG = ρsubstance/ρH_2O. Finally, porosity (Po) is a measure of void space within the stone and was measured using the formula Po = VV/VT [24].

Chemical analysis

Qualitative and quantitative analyzes of water-soluble salts have been performed using heat loss analysis, acid loss analysis and sieve analysis called simple chemical analysis. For heat loss analysis, samples prepared by very fine grinding were placed in porcelain crucibles weighing 500 mg. Samples in porcelain crucibles were held in a muffle furnace at 105 °C, 550 °C and 1050 °C for 2, 1 and 30 h, respectively. After each heat treatment, the samples were cooled in a desiccator and weighed. The moisture content, heat loss at 550 °C, and amount of calcium carbonate of the samples were calculated from the

Table 1 Photographs showing the places where the samples were taken from the building and information about the samples

No	(a)	(b)	(c)	(d)
1				It is a sample of joint mortar which has white-colored, sporadic organic (botanic) particles, plenty of lime lumps of 1-3 mm in size, aggregates up to 3 mm, generally 1 mm in size, the thickness of which cannot be defined, and brownish contamination can be seen on the surface, It is taken from the interior of the apse of the left nave of the Mor Yakup Church.
2				It is a sample of a joint mortar that has A cream-colored joint of unidentified thickness, in which rare organic (botanic) particles, 1-2 mm lime lumps, and abundant brown-colored aggregates up to 5 mm in size. It is taken from the east corner of the left nave of Mor Yakup Church.
3				It is a sample of a joint mortar whose thickness cannot be defined, brownish-cream colored, with sporadic organic (botanic) fragments, plenty of lime lumps, abundant aggregates smaller than 0.5 mm, and brownish pollution on the surface. It is taken from the west corner of the north facade of the left nave.
4				White colored organic (botanic) fragments, copious amounts of lime pellets, aggregates smaller than 0.5 mm, white colored 4-colored organic (vegetable) fragments taken from the front arches of the main nave liturgy section of the Mor Yakup Church, a black colored layer can be seen on the surface. It is a sample of plaster with a thickness of 5 mm.
5				White colored, sporadic black organic (vegetable) particles, plenty of lime pellets, aggregates smaller than 0.5 mm, black colored on the surface, taken from the left of Sample 4 from the front arches of the main nave liturgy section of the Mor Yakup Church. It is a sample of plaster with a thickness of 4-5 mm with one layer visible.
6				It is a cream-colored plaster sample of 6-7 mm thick, which was taken from the interior of the apse of the left nave of the Mor Yakup Church, with lime lumps, sporadic aggregates up to 0.2 mm in size, and a brownish black colored slippery layer on the surface
7				It is a stone sample of a whitish cream-colored stone with sporadic grayish lines and dark cream-colored dirt on its surface, taken from the front arches of the main nave liturgy section of the Mor Yakup Church (from the same place as Sample 4).
8				It is a white stone sample taken from the left part of the north façade abutment of the main nave of the Mor Yakup Church, with crystalline particles in its content and a cream-brown dirt layer on its surface.

(a) The structural element from which the sample was taken, (b) Local area of which the sample was taken, (c) sample examined in the laboratory, (d) Explanatory information about the sample

weight difference. A qualitative and semi-quantitative analysis of mortar-damaging water-soluble salts (chlorine, sulfate, nitrate, carbonate, etc.) was performed. Total salt content was evaluated with measured conductivity values. For each mortar sample, a stock solution was prepared (0.50 g sample, 50 ml deionized water) and the dissolved salts in water were analyzed for conductivity measurements. For acid loss and sieving analysis, the sample binding matrix was reacted with 10% HCl acid, silica aggregates and other insolubles were separated at the end of the process, and the acid loss rate was calculated. At the end of the acid loss analysis, a sieve analysis was performed on the remaining aggregates to calculate their size and abundance. Then, using a stereoscopic optical microscope, the type, size, color, content, and average abundance of these aggregates were measured. Dried samples of 25–50 g were reacted with HCl acid to dissolve the binding matrix, the insoluble portion was filtered, washed and dried again in an oven at 105 °C. Silica agglomerates that remained insoluble in acid were passed

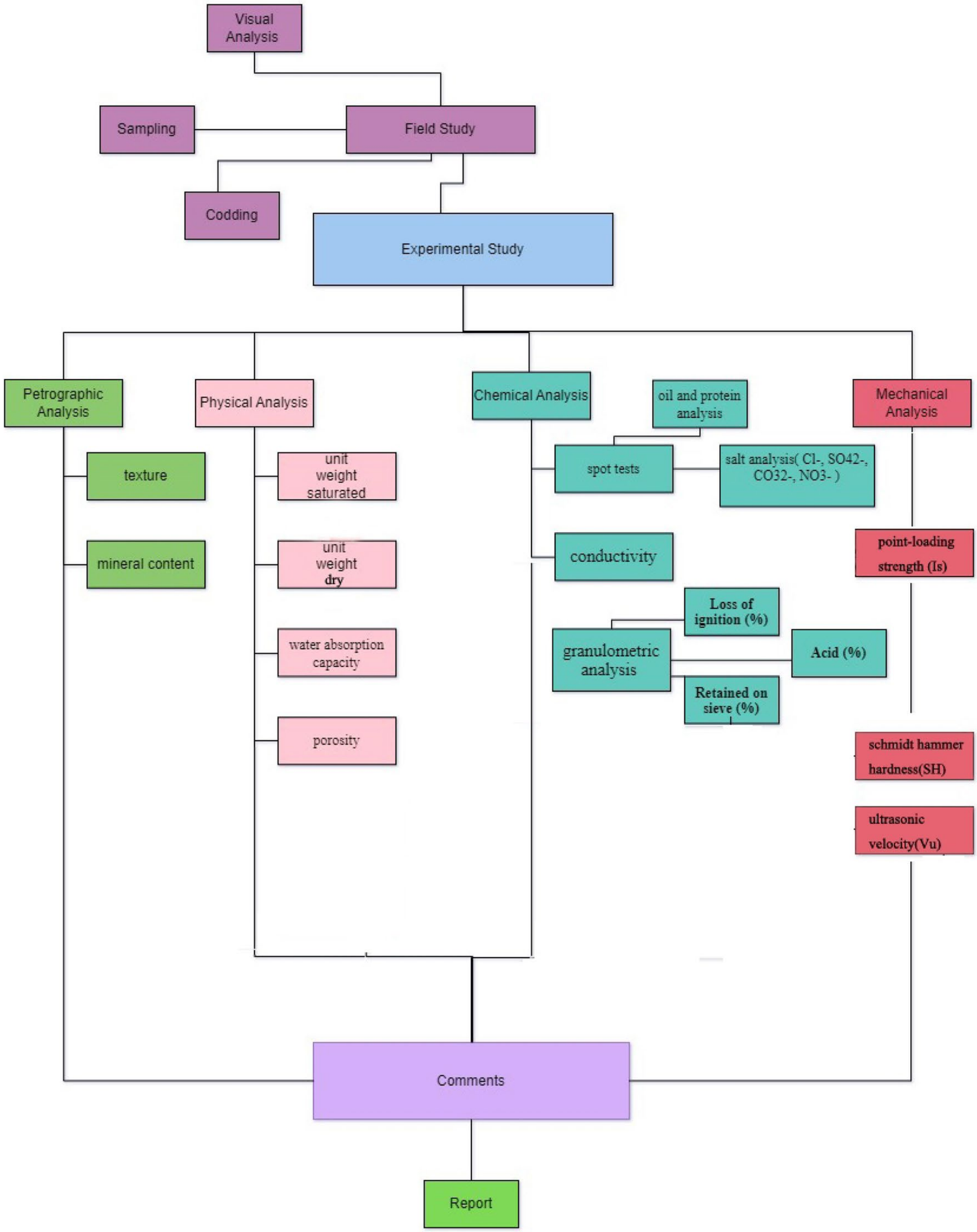

Fig. 4 Flow chart of the steps followed in the methodology for characterizing the materials of the building and determining the material strength problems

through 125, 250, 500 and 1000 micron and 2.4 and 8 mm sieves. Visual analysis was performed under a stereomicroscope on aggregates of various sizes that passed through the sieves [24–27].

Mechanical analysis

Schmidt Hammer (SH), an inexpensive, fast and convenient non-destructive method, was used for information on surface rebound hardness related to compressive strength. The hammer is pressed against the rock surface. The hammer has a springy mass that oscillates against a piston. The piston acts on the rock surface and the mass thrusts, the rebound value of the mass is measured [28].

With the ultrasonic velocity (UV) method, the propagation changes of the ultrasonic velocity wave in the rocks were analyzed. This method, which makes it possible to examine material homogeneity, can be considered as important methods in the evaluation of natural stone structures. UV equipment consists of a receiver, transducer and a display. The gauge represents the travel time from the transducer to the receiver. The equation for determining the impact velocity; V = L/T where V: speed (km/h), L: path length (cm), T: transit time (μs). Ultrasonic device produced by consuming high frequency sound was used in this experiment. Measurements were made indirectly from the same surface. If the material is hollow, has low density and/or has cracks in it, the sound transmission rate is low. The sound transmission velocity and the homogeneity of the materials can be compared, the surface hardness has been evaluated together with the test results, and its strength has been estimated [28].

In addition, the point load test method was used to determine the strength classification of the rocks. Core specimens (for diametrical and axial tests), cut block specimens or irregularly sized specimens can be used in the point loading test. The rock samples, whose dimensions are measured and placed between the conical tips, are broken within a certain period of time and the failure load is read from the load indicator. Using the load (P) and sample sizes (D, W) obtained from the point-loading test, first the uncorrected point-loading strength (Is) is found. In order to find a standard point loading strength index (ls), the Is value was corrected by the method proposed by ASTM [29]. Finally, based on the results obtained, Bieniawski [30] classification of rocks according to point load strength, the strength classification of the rocks used in this study was evaluated. According to this classification, if the Is_{50} value is less than 1, it is classified as very low resistant, 1–2 low resistant, 2–4 medium resistant, 4–8 high resistant, and higher than 8 high resistant rocks.

Results

Results of visual analysis

Since the building was restored at regular intervals in the past, it has reached today by preserving its structural integrity. Visual examinations shows that cement-based applications done on the building in the pasts are the most faulty restoration applications. In addition, ıt was determined that the main deterioration types in the materials of the building were erosion, fractures, loss of parts and the dissolve of the joint mortars between the masonry work on the facades. On the interior walls and burial chambers of the building, original plaster residues that have survived to the present day show bursting and peeling (Fig. 5).

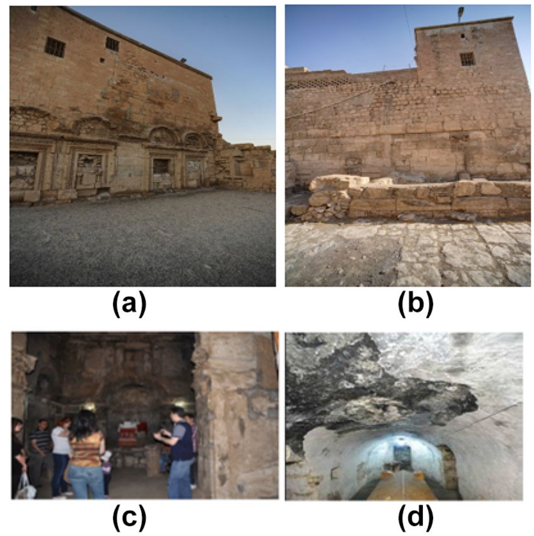

Fig. 5 Some sample images of material deterioration in the building, **a**, **b** Efflorescence, erosion, fractures, loss of parts and the dissolve of the joint mortars between the masonry work on the facades, **c** Faulty cement-induced restoration applications in the interior walls of the building, **d** bursting and peeling on the original plaster

Table 2 Ratio of total aggregate/binder content in the matrix of mortar and plaster samples

Sample no	Matrix total binder (%)	Matrix total aggregate (%)
1	91	9
2	87	13
3	88	12
4,5 Top layer	93	7
Sublayer	90	10
6 Top layer	97	3
Sublayer	95	5

Petrografik Analiz Sonuçları

The textural and aggregate/binding properties of the samples prepared for thin-section optical microscope analysis were examined under a stereo microscope, and the mineral contents and ratios of thin sections were examined under a polarizing microscope and the results are shown in Tables 2 and 3. Optical microscope examinations revealed that the plaster samples have a

Table 3 Substances in the matrix binder content of mortar and plaster samples (lime/clay/cement) and minerals/additives in the aggregate content

Sample no	Matrix binder content (100%)					Matrix aggregate content (100%)		
	Lime (C)	Limestone	Clay	Cement	Plaster	Rocks and minerals*	Brick fracture	Organic content
1	100	–	–	–	–	100 (Q,Pl,K,Op)	–	–
2	100	–	–	–	–	100 (C,Q,K,Op)	–	–
3	90	–	10	–	–	99 (Q,K,Op,C)	1	–
4, 5 Top layer	100	–	–	–	–	99 (Q,K,Op)	1	–
Sublayer	100	–	–	–	–	99 (Q,K,Op)	–	1
6 Top layer	100	–	–	–	–	100 (Q,K,Op)	–	–
Sublayer	100	–	–	–	–	100 (Q,K,Op)	–	–

C: calcite, Pl: plajiyoklas, Py: piroksen, Q: kuvars, Op: opaque minerals

two-layered structure. A high amount of binder was determined in the petrographic structures of the mortar and plaster samples. The matrix total binder (%TB) content of the mortar samples varies between 87–91% and in plasters between 90–97% (Table 2).

The upper layers of the plaster samples contain higher aggregates than the lower layers. Lime constitutes the binding structure of the mortar and plaster samples, all of which have unique characteristics. There are brick fragments at the rate of 1% of the total aggregate in the aggregate structure of the upper layers of Sample 3 from the mortar samples, and Sample 4 and Sample 5 from the plaster samples. In addition, organic additive parts (at the rate of 1% of the total aggregate) were determined in the structure of the lower layers of the same plaster samples. Mortar samples are richer in aggregate content than plaster samples. On the other hand, rounded and broken/angular aggregates are found together in plaster samples.

Quartz (Q), limestone (K) and opaque minerals (Op) constitute the aggregate content in plasters. Lime is the most abundant component in the binder content of mortars and plasters. In Sample 3, the binder content mixed with a small amount of clay minerals spread and dispersed in the mortar. In addition, the petrographic results showed that the rocks and minerals forming the aggregate in the mortars were associated with Calcite (C), Quartz (Q), Limestone (K), small amounts of opaque minerals and rare amounts of plagioclase minerals (Table 3).

The rock structures were determined by petrographic examinations of the stone samples (Sample 7 and 8) sampled from the building. Accordingly, Sample 7 has limestone (sparitic texture) and Sample 8 has travertine type ski structure. Travertine in the rocks presents a more porous structure than the sample limestone. Sparitic Limestone (Sample 7); The hardness (Mohs) value is 2.5–3, and the calcite-containing (3%) porous rock structure is complemented by calcite as well as quartz and opaque minerals. There are occasional aragonite mineral deposits in the cavities in the structure. The hardness (Mohs) value of the travertine rock type (Sample 8) is 2.5–3, and the porous (6%) rock structure formed by cold water precipitation mainly consists of calcite and aragonite minerals (Table 4). Petrographical properties of Mor Yakup Church are shown in Fig. 6.

The results of physical analysis

The basic physical tests performed to determine the physical properties of structural samples (UVW: unit volume weight, WAC: water absorption capacity, P: porosity) are as follows.

The saturated/dry unit weights of the mortars (Samples 1–3) are respectively 1.92–2.15 g/cm^3 (average 2.05 g/cm^3)/1.54–2.05 g/cm^3 (average 1.79 g/cm^3), the saturated/dry unit volume weights of the plasters (Samples 4–6) are respectively 1.80–1.99 g/cm^3 (average 1.90 g/cm^3)/1.58–1.94 g/cm^3 (average 1.76 g/cm^3). The unit volume weights of the mortar samples are higher than the plasters. The water absorption capacity and porosity

Table 4 The results of physical tests of samples (unit weight saturated/unit weight dry/water absorption capacity/porosity)

Sample no	Unit weight saturated (g/cm^3)	Unit weight dry (g/cm^3)	Water absorption capacity (%)	Porosity (%)
1	2.08	1.54	16.62	25.67
2	2.15	2.05	2.19	4.50
3	1.92	1.79	3.76	6.72
4	1.90	1.58	10.90	17.17
5	1.99	1.94	1.17	2.28
6	1.80	1.75	1.54	2.71
7	2.16	2.00	3.69	7.38
8	2.12	1.97	3.49	6.89

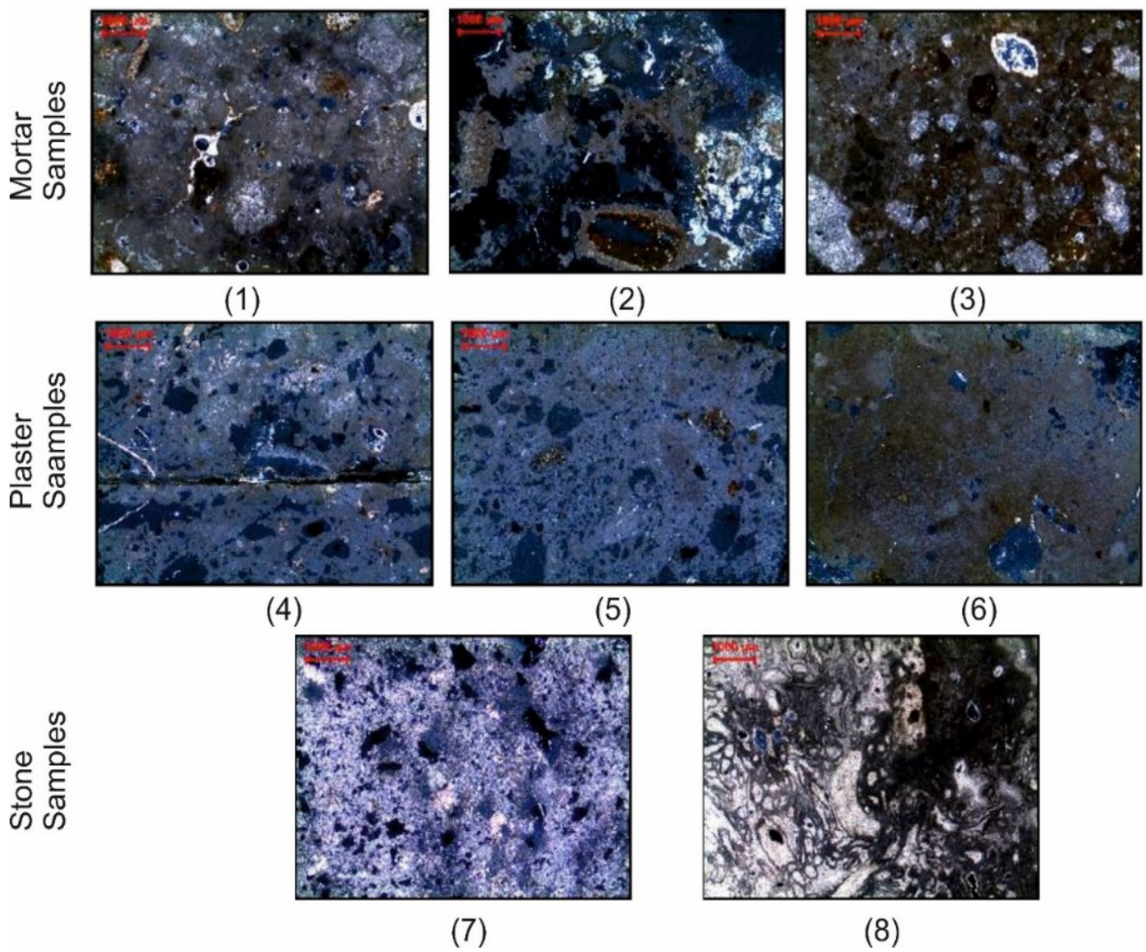

Fig. 6 Petrographic images of samples from the Mor Yakub Church. **1**–**2**–**3** The aggregates in the mortar samples have a rounded structure. Calcite (C), Quartz (Q), Limestone (K), (Op) and a small amount of Plagioclase (Pl) in the aggregate matrix are observed in the mortar samples. **5**–**6** Quartz (Q), Limestone (K), opaque minerals (Op) in the aggregate matrix of the plaster samples and organic added parts at the rate of 1% of the total aggregate in the structure of the lower layers of the samples. In addition, rounded and broken/angular aggregates are seen in the plaster samples. **3**–**4**–**5** Brick pieces are seen in the aggregate structure of the upper layers of the samples at the rate of 1% of the total aggregate

of the mortar samples are between 2.19–16.62% (average 7.52%)/4.50–25.67% (average 12.30%) respectively, and the water absorption capacity and porosity of the plaster samples are also they vary between 1.17–10.90% (mean 4.54%)/2.28–17.17% (mean 7.39%), respectively. From these findings, it is seen that mortars are more porous than plasters and their water absorption rate is higher. Samples with high unit weight and low porosity are expected to be more durable. In this context, it turns out that Sample 1 from the mortar samples and Sample 4 from the plaster samples are the samples with the lowest strength (Table 4).

Chemical analysis results

In the spot anion tests (Cl^-, SO_4^{2-}, CO_3^{2-}, NO_3^-) applied to mortar, plaster and stone samples, low amounts of sulfate (SO_4^{2-}) salting were detected in mortars and plasters, while sulfate (SO_4^{2-}) salinization was not detected in the stones. The total water-soluble salt content of the mortar and plaster samples is quite high as expected since they have lime-type binders. The total salt content in mortars varies between 6.5–18.8% (average 12.07%) and in plasters between 11.1–14.8% (average 12.93%). The total salt contents of the limestone (Sample 7) and travertine (Sample 8) stone samples were 3.1% and 3.5%, respectively. A very high amount of nitrate (NO_3^-) type salinization was detected in all of the samples. Organic additives (plant, straw, tow, etc.) were not detected in the aggregate structure of the mortar samples. While protein and oil content were not found in the mortar samples, the amount of oil was determined in Sample 4, which is one of the plaster samples. The black layer samples on the plaster were examined separately in

Table 5 Water-soluble salts, conductivity, protein and oil analyzes

Sample no	Type	Color	Cl^-	SO_4^{2-}	CO_3^{2-}	NO_3^-	Conductivity (μS)	Salt (%)	Protein	Oil
1	Mortar		+++	+	−	++	1178	6.5	−	−
2	Mortar		++++	+	−	++++	3360	18.8	−	−
3	Mortar		++++	−	−	+++	1962	10.9	−	−
4	Plaster	Black	++++	+	+	++	1994	11.1	+	−
5	Plaster	Black	++++	+	−	+++	2660	14.8	+	−
6	Plaster	Brownish black	++++	−	−	++++	2314	12.9	+	+
7	Stone		+++	−	−	++	566	3.1	−	−
8	Stone		++	−	−	+++	632	3.5	−	−

−: absence; +: small amount; ++: present; +++: abundant; ++++: excessive amount

Table 6 Granulometric analysis of aggregates with loss of ignition and acid

Sample no	Loss of ignition (%)			Acid (%)		Retained on sieve (%)					
	Moisture	550 °C	$CaCO_3$	Loss	Retained	2500 μm	1000 μm	500 μm	250 μm	125 μm	< 125 μm
1	3.27	4.93	83.07	96.67	3.33	–	3.70	38.89	25.93	12.96	18.52
2	1.88	3.79	89.03	97.28	2.72	–	–	25.00	27.50	20.00	27.50
3	8.26	7.80	88.78	97.40	2.60	–	11.90	23.81	23.81	19.05	21.43
4	10.19	10.00	43.09	93.01	6.99	–	32.58	20.22	8.99	8.99	29.21
5	13.15	9.29	54.65	98.87	1.13	–	9.09	9.09	18.18	27.27	36.36
6	9.96	16.67	72.09	99.51	0.49	–	16.67	16.67	16.67	16.67	33.33
Ort. 1–2–3	4.47	5.51	86.96	97.12	2.88	–	5.20	29.23	25.75	17.34	22.48
Ort. 4–5–6	11.10	11.99	56.61	97.13	2.87	–	19.45	15.33	14.61	17.64	32.97

terms of protein and oil contents, protein was detected in the samples. Organic additives (plant, straw, tow, etc.) were not determined in the aggregates of the mortar samples. In plaster samples, on the other hand, it was determined at a very low rate in Sample 4 and Sample 5. While protein and oil content were not found in the mortar samples, the oil value was determined in Sample 4 of the plaster samples (Table 5).

The results of the calcination (heat loss) analysis of the mortar and plaster samples at 105 ± 5 °C, 550 ± 5 °C and 1050 ± 5 °C, the proportion of silicate aggregates that did not react as a result of acid treatment, and the size distribution of these aggregates are given in Table 5. Mortar samples contain moisture content varying between 18.38–18.94%. Plaster samples (Samples 4–6; average 11.10%) are in a more humid environment than mortar samples (Samples 1–3; average 4.47%). Organic carbon content was determined between 4.44–5.52% (on average 5.51%) in the structure of the mortar samples, and between 9.29–16.67% (on average 11.99%) in the structure of the plaster samples. Organic tow (plant, straw, etc.) added to the structure of the plaster samples in order to increase the adhesion to the surface can be observed in the plasters in a way that differs from the mortars. The total carbonate content of the acidic treated mortar samples varies between 96.67–97.40% (average 97.12%), and in plasters between 93.01–99.51% (average 97.13%). Both the loss of ignition and the carbonate content determined in mortars and plasters by acidic treatment are quite high (Table 7).

Table 7 Mechanical test values of rocks (Schmidt hammer hardness (SH)/ultrasonic velocity (Vu)/Is_{50})

Sample no	Schmidt hammer hardness (SH)	Ultrasonic velocity (Vu) (km/s)	Is_{50} (MPa)
7 (sparitic limestone)	29.4	3.30	1.4
8 (travertine)	29.7	5.02	1.6

According to the results of the sieve analysis of the aggregates obtained after the acidic treatment applied to the mortar and plaster samples, while there is no aggregate over 1000 μm in mortar (Samples 1–3) and plaster (Samples 4–6) samples, coarse aggregate and a more homogeneous distribution are observed in plasters at a lower rate than mortars. In the mortar samples, the aggregate structure is composed of fine/average/coarse sand aggregates varying between 125–1000 μm. In plaster samples, a balanced aggregate distribution (125–1000 μm) is observed, with clay/silt aggregates being denser (average 32.97%, < 125 μm). The $CaCO_3$ content was determined at different rates in the coarse and thin layers of the plasters. While it was detected at an average rate of 35% in pink colored rough plaster samples; 80% $CaCO_3$ was detected in fine (glazed) plasters (Table 6).

Mechanical analysis results

The hardness of sparitic Limestone (Sample 7) (Mohs) value is 2.5–3, and the hardness (Mohs) value of the travertine rock type (Sample 8) was determined between 2.5–3. Although the limestone sample seems to be slightly more durable than the travertine sample in terms of its basic physical properties, it was determined that the travertine sample exhibited a more homogeneous rock structure compared to the limestone sample with the ultrasonic velocity measurement value. It is seen that the values for Is_{50} (point load strength index) vary between 0.55 and 8.62 Mpa. Mechanical values show that the historical stones used in the building are in the class of low strength rock [30] (Table 7).

Discussion

In this study, field and laboratory studies were carried out in order to characterize the construction materials of the Mor Yakup Church and to understand the causes of material problems, and it was evaluated which types of factors caused deterioration in the building and could pose a risk of deterioration.

Within the scope of the study, various properties related to the material characterization of the structure have been defined with petrographic analyzes at the first stage. According to the petrographical analysis results of plaster and mortars, it was seen that plaster and mortars with lime binder content were used predominantly in the construction of the church. The aggregate content of the mortars is associated with minerals from calcite, limestone and quartz, minor amounts of opaque minerals and rare amounts of plagioclase minerals. The limestone particles in the matrix come from the limestone blocks used in the building. Smaller amounts of particles also come from natural sources. Limestone aggregate amounts vary from sample to sample. In the Sample 3 which is a mortar sample, brick fragments at the rate of 1% of the total aggregate were also found (Table 3). When the content of this type of mortar is examined, it is seen that it is the traditionally used Inkara Mortar in the region. These traditional type mortars, called Inkara mortar, were frequently used in Artuqid structures [30, 31]. In addition, the brick fractures used in the binder content of the mortars are artificial pozzolanic additives used to increase strength [32]. The rounded structure of the aggregates in the mortar samples indicates that the original application was made using aggregates from the stream bed [33]. In addition, the analysis results shows that the mortars contained a small amount of clay minerals. Normally, traditional Inkara mortars do not contain clay. The presence of clays in the mineralogy of mortar samples in the building poses a serious risk for the integrity of such mortars. Clays contribute to the formation and enlargement of cracks with their swelling properties, which can cause pressure build-up in aqueous environments. In addition, the daily and seasonal changes in humidity will cause a change in the volume of the clay. Clay minerals are not very destructive due to swelling, but they cause degradation due to osmotic swelling during wet and dry cycles [34].

According to the petrographic analysis results of the stones, the main composition of the church structure is limestone and travertine. Calcite is a mineral commonly found in both construction materials. Sample-7 has limestone (sparitic texture), and Sample 8 has travertine type rock structure. Petrographic and analytical results show that the sparitic limestone (Sample 7) consists mainly of calcite-containing (3%) porous rock structure, calcite, quartz and opaque minerals, and aragonite mineral deposition in places in the cavities (Table 4). Various studies have reported that such stones with different mineral contents cause physical damage such as fractures, cracks, loss of parts, bursting as a result of the temperature differences of the different minerals in the annual and daily cycles, causing different amounts of expansion or contraction of the different minerals of the stone [6, 35–37]. In this context, due to the different thermal expansion rates of calcite and quartz in the content of the stones, it can cause many internal stresses that lead to micro cracks and fragmentation of the stones. In particular, the thermal coefficient volumetric expansion of quartz is 0.36 between 20 and 100 °C. Calcite exhibits anisotropic thermal strain behavior due to positive and negative linear thermal expansion coefficients. These different coefficients create high tensile stresses along the crystal boundaries, significantly affecting the fragmentation of stones at high temperature fluctuations on a daily and monthly basis. Similar to calcite, aragonite has different coefficients of thermal expansion [38]. Calcite dissolves in the water and reacts with outdoor pollutants whenever it is exposed to severe environmental conditions such as humidity, pollutants and heavy rains [6]. As a result of the observational examination, it is estimated that physical destructions such as breakage, crack, loss of parts, explosion, which are observed in the structure, are caused by these reasons (Fig. 5). Because, according to the climatological data obtained from the meteorology station, the monument is located in an environment where the summers are hot and dry, and it is located in a region where the effects of rain precipitation and high temperature fluctuations in cold seasons [39]. In this context, as a result of all these thermal changes occurring in the region, it is concluded that the thermal stresses caused by the internal mineralogical factors of the stones and the interaction of cyclical weather conditions will lead to weakening of their durability and flexibility. These variables will provide physical deterioration of stone blocks as well as their heterogeneous structure, which increases the weathering process and speed.

Briefly, petrographic examinations of the stones show that the causes of deterioration of the stones of the building are the result of the interaction of internal defects of the stones and external environmental factors. Intrinsic factors are defined as the internal problems of construction materials related to the chemical, physical and mechanical properties of stones, and internal problems are related to the interaction between environmental conditions and the intrinsic properties of materials [35]. Nusaybin, the geographical region where the church is located, is affected by many geo-environmental conditions, especially temperature fluctuations, strong winds and humidity. The interaction of these environmental factors with internal defects caused physicochemical and mechanical damage in building materials [36].

Finding the physical properties and gap size distribution values is considered important for the repair mortar to be produced in the literature [40]. In this context, when the physical analysis results of the mortars and plasters are examined, it is seen that the mortars are more porous and the water absorption rate is higher than the plasters (Table 4). Mortars and plasters with low porosity are considered more durable [41]. In this context, mortars can be considered to be more durable than plasters. In addition, in the calcination analysis, the relative moisture content of the mortar samples was found to vary between 18.38 and 18.94%. According to these values, mortar samples are in a more humid environment than plaster samples (Table 6). In the observational analyzes, it has been determined that the joint mortars between the stone masonry on the facades have more melting and depletion in places than the plasters. This proves the fact that mortars absorb more environmental and climatic water than plasters and degrade more. When the physical analysis results of the stone samples were examined, it was seen that the unit volume weight of the limestone reached a slightly higher value than the travertine stone, and the water absorption rate of the limestone sample was lower than the travertine sample. Rocks with high unit weights are generally less porous, absorb water less, and have high specific gravity [42]. In this context, although the limestone sample seems to be slightly more durable than the travertine sample in terms of its basic physical properties, it has been determined that the travertine sample exhibits a more homogeneous rock structure than the limestone sample with the ultrasonic velocity measurement value (Table 5). In addition, the water absorption of stones is classified as low absorbent stone (1 to 10%), medium absorbent stone (10 to 50%), and high absorbent stone (50 to 100%) [43]. In this context, it is seen that the stones used in the building fall into the group of low-absorption stones. It is known that as the degree of absorption increases in stones, the mechanical strength decreases [44, 45]. All these physical studies show that the historical stones used in the building are characterized by high absorbable and dense micro-scale textures.

In the spot anion tests performed on mortar, plaster and stone, it was determined that a very high rate of chloride (Cl^-) type salting occurred in all of the samples (Table 5). Observational determinations showed that cement mortar was used to connect and fill large cracks in many of the stone blocks used in the walls of the church (Fig. 5). In addition, Cl^- ions originating from Portlant cement were found abundantly in the spot test results. Since these mortars cause condensation in areas previously repaired with cement-binding mortar-plaster-filling such as Portland, wetting is also observed in periods without precipitation, and severe stresses occur due to both condensation and thermal expansion difference during periods of high temperature change (day and night). In addition to such physical effects, Portland cement repair materials cause salinization by transferring the water-soluble salts in their contents to the trace material. In Portland cement, low vapor permeability (i.e., the ability of the material to make the movement of moisture in the vapor phase difficult) leads to the trapping of moisture, causing the accumulation of salts in the water as a result of the wetting–drying cycle, causing the materials to deteriorate [46–52]. In addition, a very high amount of nitrate (NO_3^-) salting was determined in all of the mortar, plaster and stone samples. The relevant literature reports that NO_3^- salt is generally formed as a result of acid effect caused by stone air pollution [4, 53–57].

As a result, physical damages such as erosion, fractures, loss of parts on the stones used in the building, which can be seen from the observational determinations, confirm the role of NO_3^- and Cl^- salt in the formation of melting and depletion in the joint mortars between the stonework on the facades (Fig. 5). In addition, due to the terrestrial conditions prevailing in the region, building materials are frequently exposed to wetting–drying cycles and a humid environment is formed on the stones. This situation caused the limestone stratification formed by the recrystallization of the salty waters dissolved on the stone surfaces with the effect of the microclimate, resulting in high salinity and the destructive effect of the salinization (dissolution, fragmentation). These findings support the finding of De Ferri et al. [58] that water acts as a medium for substances such as sodium and nitrate, causing fragmentation, surface erosion and cracking in the freeze–thaw or wetting–drying rings in the pores, and transporting soluble salty water, crystallization between the pores and it is seen that it triggers the get dissolving of stones. In addition, in the experimental analysis studies carried out on the basis of other provinces of Mardin, excluding Nusaybin, it was explained that the problems detected in historical stone materials in these regions were caused by the acidic effects caused by air pollution and the cement used for repair purposes in buildings due to the formation of Cl salts. These results obtained in our study, by reaching similar findings obtained in the results of this study, confirm that acid attacks affecting the buildings due to air pollution effect are high in many districts of Mardin and that the use of faulty cement in buildings is excessive [12, 14].

In the calcination analysis results of mortars and plasters, it has been shown that the total carbonate content of the acidic treated mortar samples varied between 96.67–97.40% (average 97.12%), and in plasters between 93.01–99.51% (average 97.13%). These rates seem to be quite high [59]. The reason for the high $CaCO_3$ ratio is the presence of lime binder in these samples [60]. In addition, the binder/aggregate (B/A) ratio of the mortar samples is 1/3 in the results (Table 7). In this context, these data reveal that the lime/carbonate dense binder content of the joint mortar and plaster samples of the building is not compatible with the binder: aggregate (1:2 and 1:3) content seen in traditional applications [5, 61, 62].

Conclusion

When the results of the analyzes and on-site visual analyzes are combined, it has been determined that Mor Gabriel Church consists of limestone (sparitic texture) and travertine. In addition to calcite, which is the main composition of the stones in the church structure, it contains quartz, opaque minerals and aragonite mineral from time to time. It is seen that the stones used in the building belong to the group of stones with low absorbency and are characterized by dense micro-scale textures. The stones show low values in terms of mechanical strength values. Lime is the most abundant component in the binder content of mortars and plasters. The aggregate content of the mortars is associated with minerals from calcite, limestone and quartz, minor amounts of opaque minerals and rare amounts of plagioclase minerals. It is seen that the mortar matrix is the traditional type called “Inkara mortar” used locally in the region. The reasons for the deterioration of these materials are listed and the protection methods that can be applied are suggested:

1. It is seen that the construction materials used in the building show poor physical and mechanical properties before use, since the stones contain weak minerals and mortars prone to argillization due to their formation. The reason why the stones are preferred by the local people is that they are easy to size due to these weak features and to embroider motifs on the surface. It is not possible to make any application for the conditions caused by this damage.
2. Nusaybin, the geographical region where the church is located, is affected by many geo-environmental conditions, especially temperature fluctuations, strong winds and humidity. While the monument is located in an environment where the summers are hot and dry, it is located in an area where the effects of rain precipitation and high temperature fluctuations during the cold seasons. Calcite is a common mineral in both limestone and travertine stone types, and when exposed to variable and severe environmental conditions such as humidity, pollutants and heavy rains, it dissolves in water and easily reacts with outdoor pollutants. It seems that this problem is the internal problem of the stone itself. The difference in the differential thermal expansion ratios of calcite and quartz in the content of the stones created high tensile stresses under these climatic conditions and caused many internal stresses that led to microcracks and fragmentation of stones with daily–monthly–yearly high temperature fluctuations. In summary, since the stones are weak in terms of physico-mechanics due to their internal properties, they are particularly affected by the physical environment (wetting–drying, freezing and melting of water in the pores, etc.) and suffer damages such as erosion, fractures, loss of parts and the dissolve of the joint mortars between the masonry. It is not possible to eliminate these environmental factors, but if water can be prevented from entering the content of the stone, the

problems that cause the most damage can be eliminated. In order to prevent water from leaking into the stone content, they can be protected with architectural elements to be made at their location. However, such applications are debatable in terms of technique (making a very large area closed). Another way to prevent water from penetrating into the stone is to create a water-repellent surface with some chemicals. A lot of research has been done for this, but no definite success has been achieved.

3. The presence of clays, which are not often used in traditional Inkara mortars, causes a change in the volume of the clay as a result of the daily and seasonal changes in the temperature of the area where the structure is located. This contributed to the formation and widening of cracks due to osmotic swelling during wet and dry cycles. Therefore, the osmotic swelling capacity of the church's mortars should also be taken into account during the intervention and restoration stages.
4. There is a high level of salinization in the structure, and the soluble salts in the water contained in the stones cause surface erosion in the wetting–drying cycles. Therefore, these salts and other deposits should be cleaned while soaking, paper towel closing and brushing. Since there will be more salt in the repaired parts of Portland cement, which is a very high source of chloride (Cl^-) species in observational and experimental analyzes in the structure, water-soluble salt cleaning with pulp compress should be repeated after normal cleaning. Brick fracture additive is recommended to reduce the effect of dampening and salinization. Cement-containing materials should not be used at any stage of the repair mortar and plaster. In addition, it was estimated that high amount of nitrate (NO_3^-) salting in the structure was caused by the acid effect caused by air pollution. Brick fracture additive in the mortar content is recommended both for compatibility with the original material and for reducing the effect of humidity and salting in these parts. In this context, calcium-rich lime binders should be used for the protection and even restoration of the parts of the building built with lime in the reactions between lime mortars and air pollutants [5, 63]. Lime mortar consisting primarily of slaked and rested lime is recommended for mortar and plaster repairs. Lime mortars have more successful strength properties for structures in the medium and long term in terms of strength. It is also possible to use special hydraulic lime produced for restoration in a ready-to-use condition in mortar repairs.

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LK conceptualization, literature review, writing the manuscript, AA writing and editing. MY supervision, editing. All authors read and approved the final manuscript.

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Declarations

Competing interests
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