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Analysis of Stone Deterioration on the Facades of Hatuniye Madrasah

Ayşe BİÇEN ÇELİK [1], Şefika ERGİN [2*]
Murat DAL [3], İlhami AY [4]

ORCID 1: 0000-0002-9829-0100 **ORCID 2:** 0000-0002-7287-7886
ORCID 3: 0000-0001-5330-1868 **ORCID 4:** 0000-0002-3506-3234

[1] *Dicle University, Institute of Science and Technology, Department of Architecture, 21280, Diyarbakır, Türkiye.*
[2] *Dicle University, Faculty of Architecture, Department of Architecture, 21280, Diyarbakır, Türkiye.*
[3] *Munzur University, Faculty of Fine Arts, Design and Architecture, Faculty of Architecture, 62000, Tunceli, Türkiye.*
[4] *Hakkâri University, Çölemerik Vocational School, Department of Architecture and Urban Planning, 30000, Hakkâri, Türkiye.*
**** e-mail**: sefika@dicle.edu.tr*

Abstract

The durability of natural stone in traditional buildings is important for the structures to survive today. External environmental factors have negative effects on natural stone materials. When the material is exposed to negative factors, deterioration occurs in the stone. It is important to determine this deterioration and its causes correctly and to offer solutions for the transfer of buildings to future generations. Failure to identify the factors that cause deterioration leads to the growth of damages and the formation of new damages. Determining the deterioration on the surfaces of Hatuniye Madrasah and its causes will be useful in terms of preventing problems and making the right interventions. As a result of the analyses, the types of deterioration that occurred on the facades of the building and the changes in the chemical properties of the stone according to the results of the XRF chemical analysis were determined.

Keywords: *Hatuniye Madrasah, stone decomposition, XRF analysis method.*

Hatuniye Medresesi Cephelerinde Meydana Gelen Taş Bozunmalarının Analizleri

Öz

Geleneksel yapılarda doğal taşın dayanıklılığı, yapıların günümüze kadar ayakta kalabilmesi için önemlidir. Dış çevre faktörlerinin doğal taş malzemeler üzerinde olumsuz etkileri vardır. Malzeme olumsuz etkenlere maruz kaldığında taşta bozulmalar meydana gelmektedir. Bu bozulmaların ve nedenlerinin doğru tespit edilmesi ve çözüm önerilerinin sunulması yapıların gelecek nesillere aktarılması için önemlidir. Bozulmaya neden olan etkenlerin tespit edilememesi hasarların büyümesine ve yeni hasar oluşumlarına yol açmaktadır. Çalışmada Hatuniye Medresesi'nin yüzeylerindeki bozulmaların ve nedenlerinin tespit edilmesi, sorunların önlenmesi ve doğru müdahalelerin yapılması açısından faydalı olacaktır. Yapılan analizler sonucunda yapının cephelerinde meydana gelen bozulma türleri ve XRF kimyasal analiz sonuçlarına göre taşın kimyasal özelliklerindeki değişimler tespit edilmiştir.

Anahtar kelimeler: *Hatuniye Medresesi, taş bozunmaları, XRF analiz yöntemi.*

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1. Introduction

Mardin has historically been home to many civilizations due to its location on important trade routes and its geography. The existence of the city is associated with Persian and Roman legends (Çağlayan, 2018). Throughout history, people from different cultures, civilizations, nations, languages, and religions have lived together in peace (Alioğlu, 1989). Islamic rule in Mardin began in the 7th century. In the 12th century, the Artuqids dominated the region and Mardin was the capital of the Artuqids for about 300 years.

The civilizations that lived in Mardin built structures such as mosques, madrasahs, pavilions, churches, monasteries, and tombs in the city. Some of these buildings have survived to the present day. Some of these buildings were used for two or three different functions and are still in use today (Uyar, 2019). Madrasahs have an important place among these works that have survived to the present day in Mardin. Madrasahs, which are among the historical buildings that have survived to the present day, have historically served as educational and cultural institutions (Yardımlı, 2018). Like other historical buildings, madrasahs have survived to the present day by changing in form and function.

Limestone was used in the traditional buildings of Mardin. Limestone deteriorates over time due to internal or external factors (Semerci, 2017). Deterioration can occur due to factors such as adverse climatic conditions, traffic density, and user error (Öcal, 2010; Dal & Öcal, 2013a; Dal & Öcal, 2013b). Each type of deterioration that occurs in a building prepares the environment for another type of deterioration. For example, capillary cracks from heat shock, and seeds carried by birds or insects combine with rainwater to form plants. Dust particles carried by the wind also cause the outer surfaces to erode over time. Degradation is caused by adverse environmental conditions and the rock structure to which the structure is exposed (Price, 1995; Ergin, Gökdemir, Yardımlı & Dal, 2022). Taking steps to prevent these degradations from occurring is effective in reducing damage. If adequate precautions are not taken to prevent damage to the artefact, it leads to serious destruction of the structure over time. It is important to identify the deterioration of cultural heritage buildings, understand their causes, and take appropriate measures to pass them on to future generations (Douglas, Hughes, Jones & Yarrow, 2016). The causes of each degradation and the preventive measures against the factor causing this degradation are different. For this reason, it is important to determine the deterioration with an accurate examination (Dal & Öcal, 2017). As a result of visual analysis, it is necessary to identify and classify the abrasions that occur on the structure. For example, air pollution causes chemical decay in rocks and algae forms in structures that interact with water. This deterioration can be remedied over some time and damage can be prevented. Appropriate solutions should be considered for the conservation design applied to the building. Regularly inspecting the building, choosing the stone materials used correctly, paying attention to the cleanliness of the building, and increasing the robustness of the building help to transfer the building to future generations (Doehne & Price, 2010; Dal & Yardımlı, 2021). The study examines the types and causes of deterioration on the facade surfaces of Hatuniye Madrasah. Changes in the chemical properties of the stones on the facade surfaces were analyzed by measuring them with X-Ray Fluorescence Spectroscopy (XRF chemical analysis method). The study is intended to provide an important basis for the identification of existing problems and their causes in terms of repair interventions.

2. Material and Method

In this study, the deterioration of the facade surfaces of the Hatuniye Madrasah in Mardin is discussed. The deterioration of the stone surfaces was analyzed and the types and rates of deterioration, their diversity, and causes were determined. This study covers the analysis of the courtyard facade and exterior facade surfaces of the building exposed to external environmental conditions. Hatuniye Madrasah has survived to the present day with functional changes by preserving and preserving a large part of its structural integrity.

The study was conducted using the internationally recognized mapping method. In the mapping method, deterioration was identified and classified (Fitzner, Heinriches & Kownatzki, 1997). For the mapping method used on the facades, the deteriorations occurring in the structure were identified and the deteriorations were processed on the facades with AutoCAD 2018 and Adobe Photoshop CS6 programs. The deterioration was analyzed as physical, chemical, biological, and anthropogenic deterioration (Tokmak & Dal, 2020). As a result of observational analysis, the degradation of the chemical structures of the stones that were degraded was analyzed and examined by X-Ray Fluorescence Spectroscopy (XRF chemical analysis method). The degradations occurring in the structure selected in the study indicate the proportions of different elements in the stone by using the XRF chemical analysis method after the visual analysis method. These elements are Mg, Zn, Ca, S, V, V, Mn, Co, Ni, Al, Cu, Fe, Si, P, Cr, Cl, P K, and Ti. Along with these elements, the ratios of MgO, Al_2O_3, ZnO, SO_3, P_2O_5, MnO, CuO, SiO_2, Fe_2O_3, NiO, CaO, CoO, K_2O, V_2O_5, Cr_2O_3 and TiO_2 compounds in the stone were determined, evaluated and analyzed with tables and graphs.

2.1. Study Area Features

2.1.1. History of Mardin Province

The name Mardin was first used as "Maride" by the historian Ammianus Marcellinus in the IVth century (Gabriel, 1940). The name Mardin is known as Mâridin among Arabs and Mârdê among Assyrians (Noyan, 2008; Yousif, 2011). In addition, the province of Mardin is geographically located in the north of the Mesopotamia region, which is characterized as the 'Fertile Crescent' and has fertile soils. It has been home to different cultures and ethnic origins throughout history due to its location on an important transit route and its geography and topography suitable for defence (Alioğlu, 2000).

When the first settlements of Mardin city are examined, artefacts are found until 3000 BC (Aydın, Emiroğlu, Özel, & Ünsal, 2000). In the following years, it was subjected to civilisations such as Huris, Mitanni, Assyria, Medes and Babylonians (Yıldız, 2007); after the Islamic domination, it was under the rule of Umayyads, Abbasids, Hamdanids and Marwanids (Aliveya, 2007) and Artukoğlu under the Great Seljuk Empire (Biçen Çelik, 2021). It can be said that the architectural identity of Mardin was determined during the Artuqid rule in the XIIth century (Dal & Öcal, 2017). After the Artuqids, the city came under the rule of Karakoyunlular, Akkoyunlular, Safavids and finally, the Ottomans (Çağlayan, 2018) and all civilisations left traces (Dolapönü, 1972). While some of these works have survived to the present day, some of them have not survived to the present day due to various reasons. Hatuniye Madrasah was built in the XIIth century and is among the religious buildings that have survived to the present day (Alioğlu, 2000).

2.1.2. Geographical characteristics of Mardin Province

Mardin is located in the Southeastern Anatolia Region of Turkey, on 36^{o} 54' and 37^{o} 47' north latitudes and 39^{o} 55' and 42^{o} 41' east longitudes. The city neighbouring Syria together with the provinces of Şanlıurfa, Diyarbakır, Batman, Şırnak, and Siirt. Mardin Castle is located in the highest region of the city. It is observed that the first settlements of the city were around the castle (Karataş, 2018). With the increase in the population, settlements started to move out of the castle. There were settlements towards the lower parts of the castle and east-west direction. Since the northern part of the mountain was not suitable for settlement and the south was more suitable for settlement, the city was settled on a high plateau overlooking the Mesopotamian plain (Figure 1). This area where the settlement is located has a sloping terrain. The streets here consist of stairs and steep ramps (Bekleyen, Dalkılıç & Özen 2014).

When we look at the climate of Mardin province, we see a continental climate in the centre and a Mediterranean climate in the districts. Winter months are cold. In the summer season, it is dry and hot due to the effect of the pressure and wind coming from the desert. Looking at the annual average temperature values of the province, it is seen that the highest temperature value is 29.8 ^{o}C in July and the lowest temperature value is 3.0 ^{o}C in January (Table 1). When the climatic data of Mardin province between 1941 and 2022 are analysed, it is seen that the maximum average sunshine duration is 12.4 hours in July and the minimum sunshine duration is 4.5 hours in December. Due to the climatic characteristics of Mardin province, degradation of stone material will show its effect more (Karataş, 2018).

Figure 1. Mardin's location in Turkey and Mardin view (Biçen Çelik, 2019)

Table 1. Mardin Province meteorological data evaluation (Measurement Period 1941-2022) (General Directorate of Meteorology, 2023)

MARDİN	Ocak	Şubat	Mart	Nisan	Mayıs	Haziran	Temmuz	Ağustos	Eylül	Ekim	Kasım	Aralık	Yıllık
Ortalama Sıcaklık (°C)	3,0	4,2	7,9	13,5	19,5	25,6	29,8	29,6	25,3	18,6	11,1	5,4	16,1
Ortalama En Yüksek Sıcaklık (°C)	5,8	7,4	11,6	17,4	24,0	30,6	35,0	34,7	30,1	22,9	14,5	8,2	20,2
Ortalama En Düşük Sıcaklık (°C)	0,6	1,4	4,6	9,8	15,1	20,3	24,6	24,7	20,8	14,7	8,1	2,9	12,3
Ortalama Güneşlenme Süresi (saat)	4,5	5,1	5,9	7,3	9,7	12,1	12,4	11,4	10,3	7,7	5,9	4,4	8,1
Ortalama Yağışlı Gün Sayısı	12,11	10,61	11,70	10,28	7,35	1,54	0,48	0,24	0,70	5,12	7,66	10,80	78,60
Aylık Toplam Yağış Miktarı Ortalaması (mm)	115,9	103,2	97,7	81,1	47,3	6,5	3,2	2,3	4,0	33,8	71,9	108,7	675,6

2.1.3. Architectural characteristics of Hatuniye Madrasa

Hatuniye Madrasah is located in Gül Neighbourhood. The madrasah was built during the reign of Kudbettin İl Gazi, the 2nd Artuqid sultan. There are the graves of Kudbettin Il Gazi and his mother Sıtti Raddviye in the madrasah. The building has not survived to the present day with its originality and has been intervened in different years. The entrance of the building has been changed. According to the existing remains, the building belongs to the group of madrasahs with two iwan courtyards extending in the north-south direction. It is understood that it has two storeys according to the remains. The building consists of a tomb, harim, and rooms. There are four rooms in the west and one room in the east; a tomb in the southeast and a harim in the south. The rooms on the west side of the building do not have windows facing the outside and the lighting is provided by the door in the portico. There is a 90x110 cm window in the room in the east direction. Two windows are measuring 100x140 cm in the place used as a tomb. The entrance to the tomb is through the door located in the northeast part of the iwan used as a masjid. The tomb section consists of a tromped dome. The interior of the building is illuminated by two windows, one on the east of the south wall and the other on the south of the east wall. There is an inner courtyard in the north of the building. The second courtyard is located in the south of the building and entrances are provided from here. The inner courtyard of the building was used as a courtyard with porticoes in the past, but in later restorations, the porticoes were covered with walls and the harim, tomb, and mosque sections were added (Figure 2). Although the building was originally two-storeyed, there is no information about how the upper floor was reached as a result of the changes (Altun, 1971; Erdal, 2020).

Limestone was used as the main material of the building. The building has a total of six facades, one on the south facade, one on the east facade, and four facades facing the inner courtyard. Cut stone and cabochon stone were used together on the facades of the madrasah (Figure 3).

3. Findings and Discussion

For cultural heritage, the factors that cause the degradation of stone material are important (Karataş & Perker, 2023). Stone has always maintained its place by changing its shape and function from the past to the present (Tintin, 2012). The first people used the stone for defence purposes, and in later periods, it was used in areas such as future messages and graves. It was also used as housing, decorative products, and symbols. The number of buildings in which stone was used and which have survived to the present day is very few (Sabbioni & Cassar, 2012).

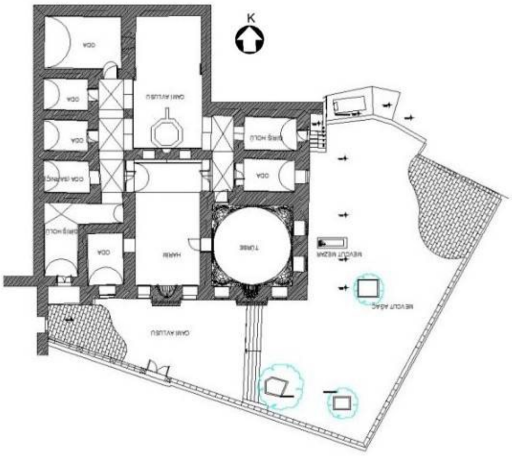


Figure 2. Hatuniye Madrasah plan (Promim Architecture Archive)

Figure 3. Hatuniye Madrasah facades (Biçen Çelik, 2019)

Limestone is one of the building materials that have been used continuously from past to present (Semerci, 2008). Limestone has different chemical and physical properties depending on the region where it is quarried. In Mardin, which is the study area, there are quarries in Ömerli, Kabala, Kızıltepe, and Midyat districts and the properties of the stones in these quarries vary (Semerci, 2008; Küçükkaya, Dal & Umaroğulları, 2006; Ergin, Çelik & Dal, 2020a). It is important to know the physical and chemical properties of limestone to select it in line with the needs of the place where it will be used (Biçen Çelik, 2021).

The stone used as a building material undergoes degradation due to climatic factors such as pressure, temperature, and wind, natural factors and external factors such as human effects (Dal, 2016). As a result of these degradations, the strength of the stone decreases considerably compared to its initial strength. To prevent the degradation of stones and to transfer them to future generations correctly, it is necessary to identify the degradation of the stone and take measures accordingly (Hasbay & Hattap, 2017; Tabasso Laurenzi, 1993). In addition, these degradations cause the formation of another degradation and in some cases accelerate the degradation process (Ergin, Çelik, & Dal, 2020b). In case the necessary precautions are not taken or incorrect applications are made, serious damages and severe destruction occur in buildings (Doehne & Price, 2010; Torraca, 1976; Yardımlı, Hattap, Khooshroo, & Javadi, 2017).

The degradation of structures can be handled in four groups as physical, chemical, biological, and anthropogenic degradation. Physical deterioration is the deterioration that occurs on the surface of the stone as a result of mechanical effects. These can be exemplified as fracture, crack, piece breakage, deformation, abrasion, cut, and honeycombing (Tokmak & Dal, 2020; Dal, 2021).

Chemical degradation is the type of degradation that occurs on the surface of the stone as a result of atmospheric events. Examples such as colour change, salting, crystallisation (blooming), crusting, blistering, sugaring and foliation are examples of chemical degradation (Öcal & Dal, 2012; Ergin, Karahan & Dal, 2020).

Biodegradation is the type of degradation caused by organic substances on the surface of the stone. Moss formation, plant formation, and bioaccumulation are among the types of biodegradation (Rivera, Ramos, Sánchez & Serrano, 2018; Dal, Zülfikar & Dolar, 2020; Dolar & Yardımlı, 2017).

Anthropogenic degradation is the degradation caused by human destruction. Improper application, misuse and periodic wear can be given as examples of anthropogenic degradation (Hattap, 2002).

In this research, the deterioration of Hatuniye Madrasah was examined under three different headings: visual examination, examination using the mapping method and examination using the XRF chemical analysis method.

3.1. Visual Investigation of the Deterioration Occurring in Hatuniye Madrasah

The deterioration of the Hatuniye Madrasah consists of physical, chemical, biological and anthropogenic deterioration. Due to the environmental and internal conditions of the limestone used as the main material of the building, the structure suffered from fragmentation, joint discharges (Figure 4a), capillary cracks (Figure 4b) and abrasions due to the effect of dust carried by the wind (Figure 4c, 4d).

Chemical deterioration types such as salination, discolouration and bacterial growth were observed in Hatuniye Madrasah. The discolouration was observed on the inner courtyard façade (Figure 5a) and the main façade (Figure 5b). Salting (Figure 5c) and bacterial growth (Figure 5d) were also observed.

Plant formation is encountered as biological degradation in Hatuniye Madrasah. The plant formations on the south and east facades of the building are shown in Figure 6.

As a result of anthropogenic effects, degradation due to the use of sharp tools was observed in Hatuniye Madrasah (Figure 7).

Figure 4. Physical deterioration of Hatuniye Madrasah (Biçen Çelik, 2019)

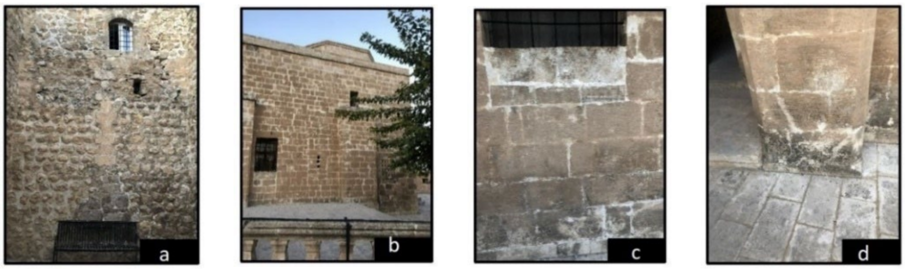


Figure 5. Chemical degradation in Hatuniye Madrasah (Biçen Çelik, 2019)

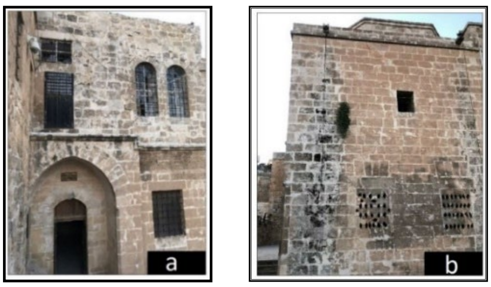


Figure 6. Biodegradation in Hatuniye Madrasah (Biçen Çelik, 2019)

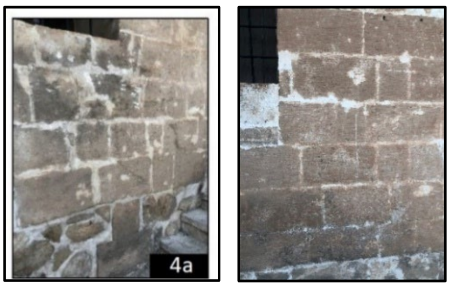


Figure 7. Anthropogenic degradation of Hatuniye Madrasah (Biçen Çelik, 2019)

3.2. Investigation of Deterioration in Hatuniye Madrasah by Using Mapping Method

The degradations occurring in Hatuniye Madrasah are shown in the charts by mapping method. When all the degradations occurring in the structure are taken into consideration, it is seen that chemical degradation is the highest and biological degradation is the lowest.

The physical deterioration in the madrasah is shown in Table 2. Joint discharge, hairline crack fragment rupture and surface abrasions are observed on the facade surfaces. It is observed that surface abrasion is the highest and fragment rupture is the lowest among the physical deterioration in the building. Surface abrasion was observed on the south, east, south-facing courtyard facade and west-facing courtyard facades of the building.

Table 2. Physical deterioration of Hatuniye Madrasah

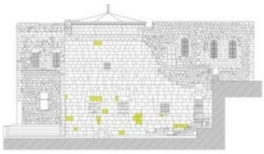
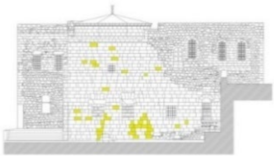
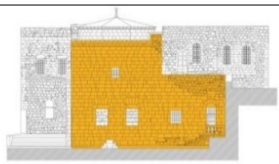
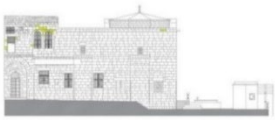
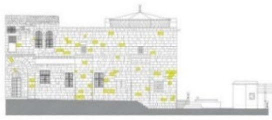
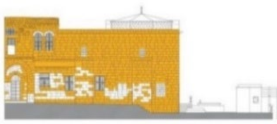
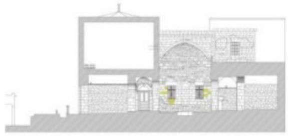
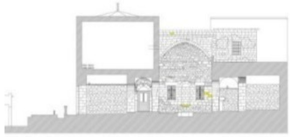
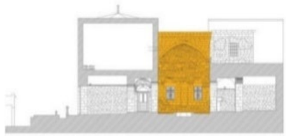
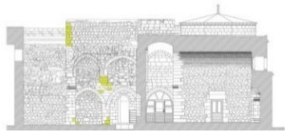
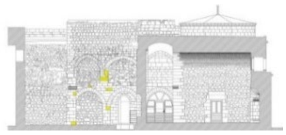
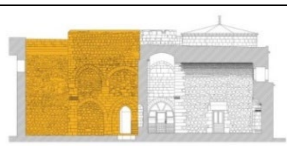
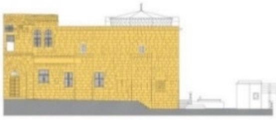
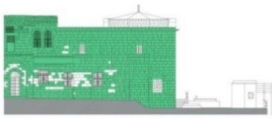
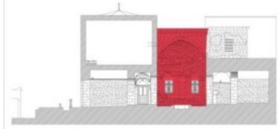
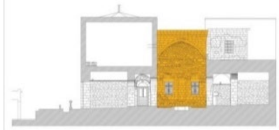
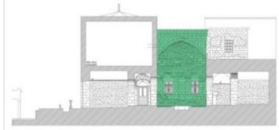
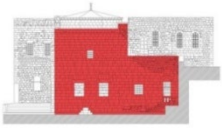
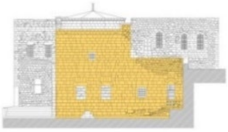
	Physical Degradation Type	Facade Deterioration Ratio	Rate (%)
EAST FACADE	Joint Discharge		1.2
EAST FACADE	Capillary Crack		2.3
EAST FACADE	Surface Abrasion		100
SOUTH FACADE	Joint Discharge		0.8
SOUTH FACADE	Capillary Crack		10
SOUTH FACADE	Fragment Breakage		0.9
SOUTH FACADE	Surface Abrasion		89
SOUTH-FACING COURTYARD FACADE	Joint Discharge		1.3
SOUTH-FACING COURTYARD FACADE	Capillary Crack		1.2
SOUTH-FACING COURTYARD FACADE	Surface Abrasion		100
WEST-FACING COURTYARD FACADE	Joint Discharge		2
WEST-FACING COURTYARD FACADE	Capillary Crack		1.4
WEST-FACING COURTYARD FACADE	Fragment Breakage		2.1
WEST-FACING COURTYARD FACADE	Surface Abrasion		100

Table 3. Chemical degradation in Hatuniye Madrasah

	Chemical Degradation Type	Facade Deterioration Ratio	Rate (%)
SOUTH FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		97

	Chemical Degradation Type	Facade Deterioration Ratio	Rate (%)
SOUTH-FACING COURTYARD FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		100

	Chemical Degradation Type	Facade Deterioration Ratio	Rate (%)
EAST FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		100

	Chemical Degradation Type	Facade Deterioration Ratio	Rate (%)
WEST-FACING COURTYARD FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		100

Table 4. Biological degradation at Hatuniye Madrasah

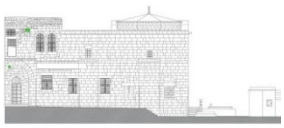
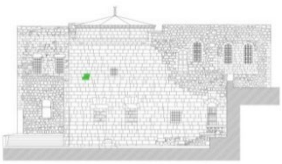
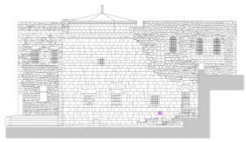
	Biological Degradation Type	Facade Deterioration Ratio	Rate (%)
SOUTH FACADE	Plant Formation		0.4
EAST FACADE	Plant Formation		0.4

Table 5. Anthropogenic degradation at Hatuniye Madrasah

	Anthropogenic Degradation Type	Facade Deterioration Ratio	Rate (%)
EAST FACADE	Sharp Instrument Use		0.1

The chemical deterioration of the building is shown in Table 3. Discolouration, salting and bacterial formation were observed on almost all of the façade surfaces. Discolouration, salting and bacterial formation were observed on all facades of the building.

Plant formation, which is a type of biological degradation in Hatuniye Madrasah, was observed on the south (0.4%) and east facades (0.4%) and shown in Table 4.

Anthropogenic deterioration in the Hatuniye Madrasah due to the use of sharp tools only on the eastern façade of the building is shown in Table 5.

3.3. Investigation of the Deterioration of Hatuniye Madrasah using XRF Chemical Analysis Method

All types of deterioration occurring in Hatuniye Madrasah were analysed with the codes determined by X-Ray Fluorescence Spectroscopy (XRF chemical analysis method). The codes determined (Table 6), the representations of the selected stones on the plan (Figure 8) and on the façade (Figure 9) are given below. The main purpose of analysing the materials of historical buildings is to obtain information about the physical and chemical composition of the materials as well as the production technology (Karataş, Alptekin & Yakar, 2022).

Table 6. Stones selected for the use of XRF chemical method for the deterioration of Hatuniye Madrasah

STONE CODE	TYPE OF DECOMPOSITION	
D0	Clean Stone	
D1a	Abrasion	Physical Degradation
D1b	Capillary Crack	
D1c	Joint Discharge	
D1d	Part Breakage	
D2a	Colour Change	Chemical Degradation
D2b	Salinisation	
D2c	Bacteria growth	
D3a	Microorganism Formation	Biodegradation
D4a	Sharp Instrument Use	Anthropogenic Degradation

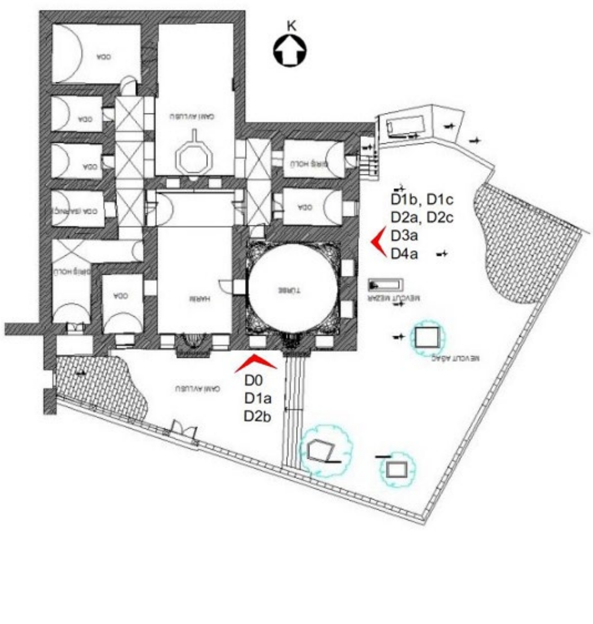


Figure 8. The plan representation of the stones selected for the use of XRF chemical method for the deterioration of Hatuniye Madrasa

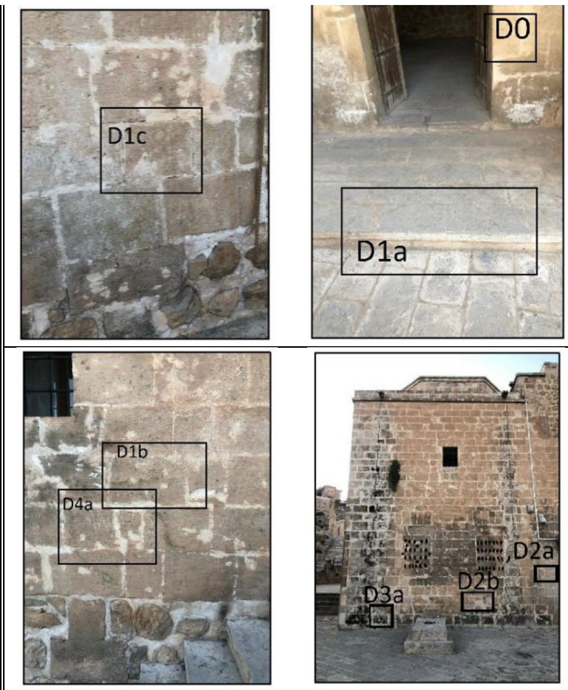
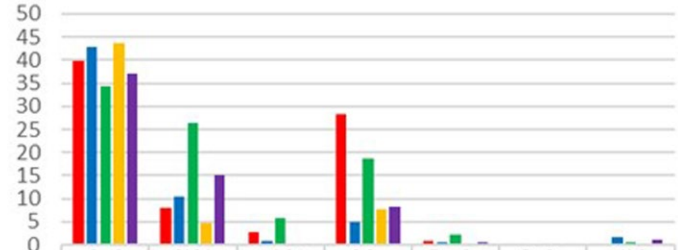


Figure 9. Demonstration of the stones selected for the use of XRF chemical method for the deterioration of Hatuniye Madrasah on the façade

The results of the analysis of the physical deterioration in Hatuniye Madrasah according to XRF analysis method are given in Table 7. According to the results of the analyses, while the SiO_2 ratio in stone D0 was 7.93%, this ratio was 26.27% in stone D1b. In addition, while the SO_3 ratio in D0 stone, which is determined as clean stone, is 28.83%, this ratio is lower in other stones. The high rate of SO_3 causes damage to the stones as a result of air pollution. No serious changes were observed in other components. In stones with different mineral contents, physical degradation such as joint failure, hairline cracks, surface abrasion, fragment breakage and fracture have been observed due to the expansion and contraction of stones due to daily and annual temperature differences (Karataş, Alptekin & Yakar, 2023).

The results of XRF chemical analyses of the chemical degradation in Hatuniye Madrasah are shown in Table 8. According to the results obtained, it was observed that the stone with the lowest SO_3 value was D2b (0.98%). While the CaO ratio is 39.87% in D0 stone, it is 24.91% in D2c stone. Another remarkable change according to the analysis results is in SiO_2. While the SiO_2 ratio was 7.93% in D0 stone, this ratio was 24.91% in D2c stone.

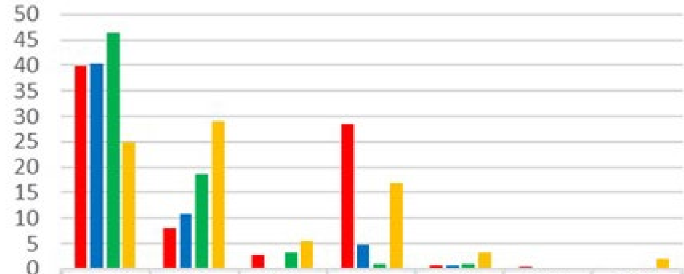
Table 7. XRF and chemical analysis results of the physical deterioration observed on the facades of Hatuniye Madrasah



	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	P_2O_5	K_2O
D0	39,87	7,93	2,73	28,38	0,74	0,36	0,14
D1a	42,93	10,42	0,74	5,01	0,67	0,17	1,69
D1b	34,19	26,27	5,88	18,73	2,11	0,14	0,62
D1c	43,54	4,78	0,14	7,62	0,39	0,029	0,39
D1d	37,01	15,11	0,27	8,3	0,68	0,031	0,97

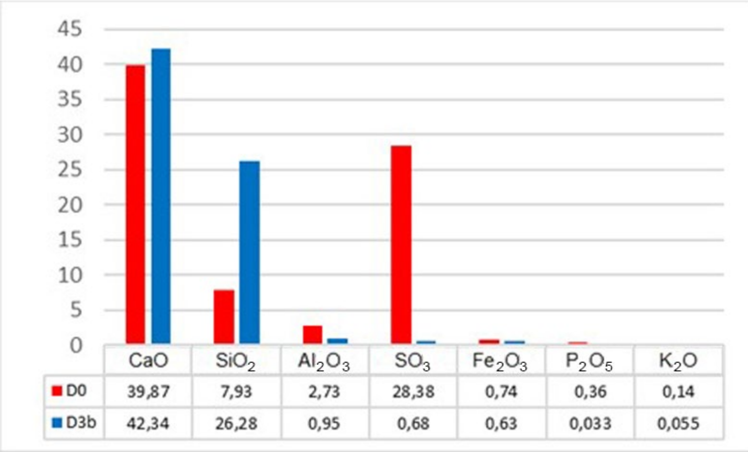
The analysis results of the biodegradation in Hatuniye Madrasah are given in Table 9. According to the results of the analyses, while the SiO_2 ratio was 7.93% in stone D0, it was 26.28% in stone D3a. Silicification of clay minerals and the development of hard layers on the surface of the stone cause the increase in the SiO_2 ratio in D3a stone.

Table 8. XRF chemical analysis results of the chemical degradation observed on the facades of Hatuniye Madrasah



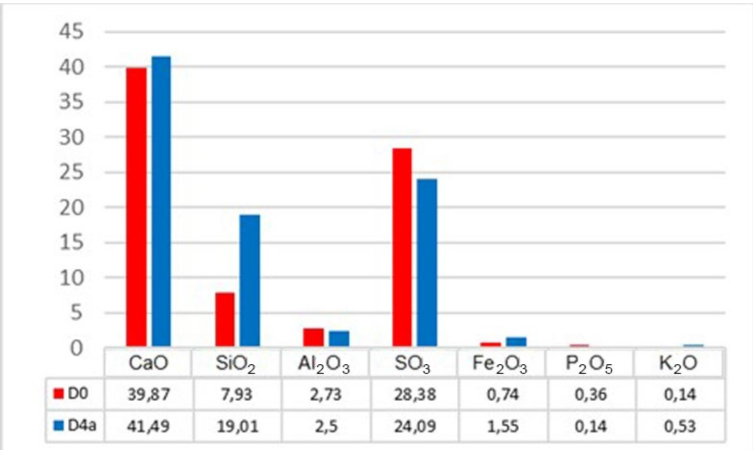
	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	P_2O_5	K_2O
D0	39,87	7,93	2,73	28,38	0,74	0,36	0,14
D2a	40,34	10,92	0,13	4,75	0,74	0,032	0,21
D2b	46,37	18,59	3,12	0,98	0,95	0,033	0,19
D2c	24,91	28,94	5,55	16,85	3,18	0,031	1,86

Table 9. XRF and chemical analysis results of biodegradation observed on the facades of Hatuniye Madrasah



When the anthropogenic degradation of Hatuniye Madrasah is analysed by XRF chemical analysis method, the ratios of CaO, SiO_2 and SO_3 components stand out. There is no significant change in the ratios of other compounds. While SiO_2 ratio was 39.87% in D0 stone, this ratio increased to 19.01% in D4a stone. While the SO3 component was 28.38% in D0 stone, it was 24.09% in D4a stone (Table 10).

Table 10. XRF chemical analysis results of anthropogenic degradation observed on the facades of Hatuniye Madrasah



4. Conclusion and Suggestions

Stone has been used in all areas of our lives by changing its shape and function from past to present. Limestone, a local stone from the Mardin region, was used as the main construction material of the building. The limestone has deteriorated over time. In this study, the deterioration of Hatuniye Madrasah in Mardin province was analysed. These deteriorations were identified through visual analysis and then grouped into specific categories. The deterioration was analysed using façade mapping and XRF chemical analysis methods.

The deterioration of Hatuniye Madrasah was analysed by mapping method. According to these analyses, it was determined that the most visible type of deterioration in the structure is chemical deterioration and the least visible type of deterioration is anthropogenic deterioration. As a result of the analyses, it can be said that the most visible type of physical degradation is surface abrasion and the least visible type of physical degradation is fragment rupture. In chemical degradation, it was observed that the most visible degradation type was discolouration and salting, and the least visible degradation type was bacterial formation. When biological degradation was considered, algae formation and plant formation were observed. As an anthropogenic degradation type, degradation was observed as a result of the use of sharp tools (Table 11).

Table 11. Deterioration on the facades of Hatuniye Madrasah

Hatuniye Madrasa	Physical Degradation				Chemical Degradation			Biological Degradation		Anthropogenic Degradation	
	Abrasion	Capillary Crack	Joint Emptying	Tool Breakage	Colour Change	Salinisation	Bacteria	Plant Formation	Moss Formation	Sharp Instrument Use	Paint Usage
South Front	+	+	+	+	+	+	+	+	-	-	-
Eastern Front	+	+	+	+	+	+	+	+	-	+	-
South Facing Courtyard Facade	+	+	+	+	+	+	+	-	-	-	-
Courtyard Facade Facing West	+	+	+	+	+	+	+	-	-	-	-

The deterioration of Hatuniye Madrasah was analysed by X-Ray Fluorescence Spectroscopy (XRF chemical analysis method). According to the results of the samples taken from the stones determined in the madrasah, the changes in CaO, SiO_2 and SO_3 values are remarkable. According to the results of the analyses, it was determined that the amount of CaO in all stone samples was higher than the number of other compounds. SiO_2 content was 28.94% in D2c stone, 4.78% in D1c stone and 7.93% in D0 stone, which is clean stone. While the SO_3 component was 28.38% in D0 stone, this ratio was found to be low in other stone samples (Table 12).

Table 12. XRF chemical analysis results of the deterioration observed on the facades of Hatuniye Madrasah

Ingredient	D0	D1a	D1b	D1c	D1d	D2a	D2b	D2c	D3a	D4a
CaO	39.87	42.93	34.19	43.54	37.01	40.34	46.37	24.91	42.34	41.49
SiO_2	7.93	10.42	26.27	4.78	15.11	10.92	18.59	28.94	26.28	19.01
Al_2O_3	2.73	0.74	5.88	0.14	0.27	0.13	3.12	5.55	0.95	2.5
SO_3	28.38	5.01	18.73	7.62	8.3	4.75	0.98	16.85	0.68	24.09
Fe_2O_3	0.74	0.67	2.11	0.39	0.68	0.74	0.95	3.18	0.63	1.55
P_2O_5	0.36	0.17	0.14	0.029	0.031	0.032	0.033	0.031	0.033	0.14
K_2O	0.14	1.69	0.62	0.39	0.97	0.21	0.19	1.86	0.055	0.53

According to the data obtained as a result of the examinations, it is observed that the amount of chemical degradation in the structure is higher. Due to the exposure of the structure to atmospheric conditions, it was determined that the amount of discolouration and salting in the structure was higher. It was observed that there was degradation caused by bacterial growths and degradation on the stone surfaces due to air pollution. According to the results of XRF chemical analyses, it was determined that as the clay and carbonate ratio increased, the degradation of the building stones increased, and the degradation decreased with the increase in the silica ratio. It was observed that calcium and silica ratios increased with the decomposition of clay minerals on the stone surface.

It is necessary to use the data and analysis results obtained from this study in the conservation projects to be carried out in the coming years and to develop solution proposals in line with these data. To stop or minimise the degradation of structures, it is important to detect structural degradation. To transfer the building to future generations, it is of great importance to accurately identify and analyse the deterioration and to eliminate them with the right solution methods.

There have been no previous studies on the Hatuniye Madrasah in Mardin. Due to the lack of studies, no comparison can be made. However, as can be seen in the master's thesis of Karataş (2018), similar types of deterioration were observed in mosque structures and madrasah structures in Mardin province. It can be said that geography and climate are effective.

Acknowledgments and Information Note

This article is derived from the Master's thesis titled "Investigation of Stone Deterioration on the Facades of Madrasa Buildings in Mardin Province and Analysis by XRF Spectrometry" completed at Dicle University, Institute of Science and Technology, Department of Architecture. The article complies with national and international research and publication ethics. Ethics committee permission was not required for the study.

Author Contribution and Conflict of Interest Disclosure Information

Ayşe Biçen Çelik contributed 40%, Şefika Ergin 20%, Murat Dal 20% and İlhami Ay 20%. There is no conflict of interest.

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