TECHNOLOGICAL PROPERTIES AND CONSERVATION PROBLEMS OF SOME MEDIEVAL BRICKS AND TILES

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

TECHNOLOGICAL PROPERTIES AND CONSERVATION PROBLEMS OF SOME MEDIEVAL BRICKS AND TILES

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The aim of this study is to examine the technology of the relatively deteriorated historic tile, brick and mortar samples of Sivas Gök Medrese and Tokat Gök Medrese. Their main deterioration factors were analyzed mainly as salt weathering. It was examined in detail, and the possible desalination methods were discussed.

For this purpose, the studies were carried out with a field survey and laboratory experiments on the two sites. Documentation of visual decay forms of Tokat Gök Medrese were done with AutoCAD.

The density and porosities of tile body and mortar samples were determined by using RILEM standards. The pore size distributions of tile and mortar samples were examined by Mercury Intrusion Porosimetry. Modulus of elasticity of tile body and mortar samples was determined and compared with the other Seljuk building materials. Mineralogical compositions of the tile body and glaze, adhesive tile mortars of Sivas Gökmedrese and Tokat Gökmedrese were analyzed with X-Ray Powder Diffraction (XRD). Their microstructure and chemical compositions were determined by using Scanning Electron Microscope coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDX).

The salts were determined for various methods such as spot tests and XRD analyses. The possible treatment methods of salt crystallization were discussed according to the properties of the examined samples.

One of the most essential causes of decay factor was salt crystallization for the two buildings which causes detachment and loss of tiles. The deteriorations were distributed over the upper and lower sides of the wall which were close to the dampness zones from the roof and above ground. The experiments proved different kinds of salts such as thenardite, sylvite, halite, natrite, nitratine and niter coming from the ground and the restoration materials such as cement based mortars. The relative humidity of the environments was compared with that of salt characteristics. It was proved that the tiles were adversely affected from salt crystallization. The best desalination method was discussed. Advection method by using poultices was based on the transformation of ions through the flowing moisture. The most prominent characteristic of the poultices must have smaller pore size distribution than original salty materials. The pore size distributions of the tiles and gypsum mortars were determined to compare and chosen the best poultice from the literature. It was concluded that kaolin-sand-based poultices having known properties was the best one as considering the pore size distribution of the tiles and mortars. The study on material properties and desalination process was expected to help different monuments having salt problem.

Keywords: Anatolian Seljuk tiles and bricks, technological properties, salt problem, desalination

ÖZ

BAZI ORTA ÇAĞ TUĞLA VE ÇİNİLERİNİN TEKNOLOJİK ÖZELLİKLERİ VE KORUMA PROBLEMLERİ

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Bu çalışmanın amacı, Anadolu Selçuklu dönemine ait olan Sivas Gök Medrese ve Tokat Gök Medrese yapılarından alınan tuğla, çini ve harç örneklerinin teknolojik özelliklerini incelemektir. Olası tuz temizleme yöntemleri tartışılmıştır.

Bu sebeple, çalışmalar arazi çalışması ve laboratuvar deneyleri olarak gerçekleştirilmiştir. Tokat Gök Medrese ana eyvan giriş cephesinin görsel bozulma haritası AutoCAD yardımı ile çizilmiş, her bir bozulma çeşidinin görece alanı hesaplanmıştır.

Çini gövde ve harçlarının özkütle ve gözeneklilik değerleri, RILEM standart test yöntemleri ile hesaplanmıştır. Çini gövde ve harçlarının gözenek dağılımları ise, civalı porosimetre yöntemi ile belirlenmiştir. Esneklik modülleri ise ultrasonic hız ölçümleri ile hesaplanarak diğer Selçuklu yapı malzemeleri ile karşılaştırılmıştır. Çini gövde ve sırlarının mineralojik kompozisyonları, X ışınları toz difraksiyonu (XRD) analizleri ile incelenmiştir. Mikro yapı ve kimyasal kompozisyonları, taramalı elektron mikroskobu (SEM) ve buna bağlı X-ışınları (EDX) analizleri ile incelenmiştir.

Görece bozulmuş olan örneklerin ana bozulma sebeplerinin, malzemenin bozunmasına ve yokolmasına sebep olan tuz kristallenmesi olduğu anlaşılmıştır. Bozulmaların yapı üzerindeki dağılımı gösteriyor ki, olası nemli bölgeler olan çatıya ve yere daha yakın bölgelerde bozulmalar fazladır. Tuz cinsleri, spot testler ve XRD analizleri ile belirlenmiştir. Tenardit, silvit, halit, natrit, nitratin ve niter tespit edilen tuzların başında gelmektedir. Yeraltı suları ve yeni onarım malzemeleri bu tuzların kaynağı olarak görülmektedir. Bu tuzların denge bağıl nemleri, bulundukları çevrelerin bağıl nem değerleri ile karşılaştırılmıştır. Bu çalışmada, çinilerin, yerden yükselen nemle ve yeni onarım malzemeleriyle gelen tuz kristallenmelerinden olumsuz yönde etkilendikleri kanıtlanmış, olasi tuz temizleme metodları tartışılmıştır.

Buna gore, en uygun tuz temizleme yönteminin, 'advektif' yöntem temelli hamurlar bazalınarak temizlenmesi olarak tanımlanmıştır. Bunun için, uygulanan tuz temizleme hamurunun en önemli özelliğinin, gözeneklerinin özgün tuzlu malzemeye gore daha küçük olması gerekmektedir. Malzemelerin gözenek büyüklük dağılımlarının belirlenmesi, en uygun gözenek dağılımına sahip olan hamurun seçilmesi ya da hazırlanması için yapılmıştır. İncelenen çini ve jipsli harçlara en uygun gözenek genişliği dağılımına sahip olan hamurlar, literatürden araştırılmıştır. Buna gore, kaolin-kum bazlı tuz temizleme hamurlarının, özgün malzemenin gözenek dağılımı dikkate alınarak en uygunu olduğu tespit edilmiştir. Bu çalışmanın, tuz problemi olan diğer yapılar için de faydalı olacağı düşünülmektedir.

Anahtar kelimeler: Anadolu Selçuklu dönemi çinileri, teknolojik özellikler, tuz problemi, tuz temizleme yöntemleri

To My Family

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INTRODUCTION

Construction and building material technologies of historic buildings are the rich architectural documents of the experiences gained over time. They are the living evidences of the architectural heritage and building materials technology. In order to conserve the original qualities of the historic buildings, the conservation interventions should be determined after the diagnostic studies of the building and its materials i.e. degree, distribution and depth of deterioration. It is also important to understand the characteristics of the building materials and technology to develop conservation treatments. Detailed studies are needed to determine the technological properties of the original materials for the development of repair materials also for the conservation applications. For the success of the conservation interventions and repairs, the temporary materials for conservation such as poultices and the repair materials such as mortars must be compatible with the original ones in terms of their visual, physical and physico mechanical properties and composition characteristics.

1.1 Definition of the Problem

During the Anatolian Seljuk period, the 13th century, Medrese buildings were constructed with characteristics including unique construction and material technologies. These have survived through the centuries coming to our times. In their interiors tiles and glazed bricks are one of the essential characteristics having historic, technological and visual properties. In addition to their visual and aesthetic values they also present the direct information about the history and technology of glazed materials belonging to the period.

The tiles were placed on the brick masonry wall by using mortars, and they were exposed to atmospheric conditions since the late 13th century (Figure 1.2). Up to the period, they were conserved due to their compatibility with the neighbouring materials on the monument and durability against environmental conditions such as frost and water. In other words they have behaved in harmony with the materials that were used together during the seasonal changes in temperature and moisture. As a result, the whole structure has survived for centuries. Gök Medrese in Sivas and Gök Medrese in Tokat are the two important examples of the late 13^{th} century medrese buildings, which are decorated with tiles. The tiles and glazed bricks coming to our times were affected from several deterioration factors in recent times. Wrong conservation interventions disrupted the harmony between the original historic materials due to their different physical and physicomechanical properties and behaving as a salt source which leading to rapid loss of tiles.

The studies on the technological characteristics and the decay forms of materials are important to conserve their original properties. For that reason, the understanding of material properties and their decay factors are crucial to study.

1.2 Aim and Scope of the Study

The aim of the study is to examine the salt deterioration problem that is developed as a result of wrong interventions such as repairs with cement mortars. For that purpose, the deterioration mechanisms of the tiles and their technological properties as macro and micro-structural changes were planned to be analyzed on the selected representative samples taken from the monuments. The data obtained was assumed to guide the conservation treatments and mainly the salt extraction. For this purpose tiles, tile mortars, bricks and salts from efflorescence zone of Sivas Gök

Medrese and Tokat Gök Medrese belonging to 13th Century were decided to be studied.

1.3 Methodology

The study is planned to include the fieldwork and laboratory work. Fieldwork is done to document the present conditions of the monuments in order to collect information about degree, distribution and depth of deteriorations of the materials. The visual deterioration forms were examined, and mapping is done for the specified facade in the fieldwork. The effects of efflorescence were easily documented on the eyvan façades of Tokat Gök Medrese. Sivas Gök Medrese was still under restoration but, the effect of restoration was detected as powdering of materials and efflorescence. Sampling on visually deteriorated sides and efflorescence zone is done after the documentation. Salts, pieces of powdered brick samples, relatively deteriorated tile and mortar samples were collected and documented on the maps. The samples on the deterioration zones and the ones on the laboratory archive were examined in the laboratory work. Their physical, physicomechanical and mineralogical properties were examined in the laboratory. The research is based on the determination of basic physical and physicomechanical properties, raw material properties, mineralogical and petrographical analyses of materials and qualitative and quantitative analyses of soluble salts of the samples. At the end of the study, the results could be used to determine the best desalination method in the literature.

1.4 General Approaches to Studies on the Properties of the Materials and Decay Problems

Bricks, tiles and their mortars are the main materials to be studied. The description of their materials and their possible decay forms are discussed. Some archaeometric studies about the materials are briefly mentioned.

Brick

Brick was the main traditional construction material for masjids and tombs before and during the Seljuk Period, and it had limited use for macrostructures as mosque and medrese buildings (Bakırer, 1981).

Bricks are the basic construction elements of historic brick masonry. The main components are brick and mortar of the brick masonry. Their surfaces may be covered with glazed bricks and tiles. Their shapes are related with the brickwork which are unit bricks and cut bricks. Unit bricks had a square shape (whole bricks), rectangular shaped (half bricks) or specially shaped as concave/convex bricks for the minarets in Islamic Architecture (Figure 1.1). Cut bricks were used for the geometric brickworks, for this reason their shapes differed according to the geometry. Glazed bricks were used extensively in the Seljuk Period. Their dimensions were the same as unglazed bricks, and had glazed surfaces (Bakırer, 1981).

There are some studies on the preparation conditions and raw material characteristics of historic bricks. Fired bricks were prepared by mixing and moulding of soil with proper composition of sand, silt and clays. It was dried slowly and fired in the drying-oven with known interior environmental conditions. During firing, mineralogical and textural changes occurred (Cultrone, Rodriguez-Navarro, Sebastian, Cazalla, Torre, 2001).

Figure 1.1 Brick units at the interior side of Sivas Keykavus Hospital (Daruşşifa), 2010

The various colors of bricks depend on the minerals in their composition, and the atmospheric conditions of the kiln. In oxidizing atmosphere brick turns into salmon pink at 900°C and reddish brown or darker red at 1100°C, since ferric oxide (Fe_2O_3) is produced due to the iron content of clay. In addition, lime in the clay produces calcium ferrite and ferric oxide which are green and red in an oxidizing atmosphere. In a reducing atmosphere, the color turns into brown or bluish color.

Clay is one of the main components of bricks and mud bricks. Particles that are smaller than 2 μm are defined as clay. Besides the definition of clay as particle size, it is also defined as a rock term. Clay is a "natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water" (Grim, 1968). They are mainly composed of silica, alumina and water. Iron, alkalis and alkaline earth materials are also present in them (Grim, 1968).

Clays have no pozzolanic character. Their pozzolanic characters are closely related to their clay content, type and heating temperature of bricks. While bricks are heated at a temperature range 600-900°C, clays gain pozzolanicity by the formation of amorphous silica and alumina and the loss of crystallographic structure. Then they can react with calcium hydroxide (Mielenz, Witte and Galantz, 1949). For this reason, the brick powders may gain the ability to react with lime if they contain pozzolanic material (Böke, Akkurt, Ipekoğlu and Uğurlu, 2006).

Kaolin, illite and smectite (montmorillonite) are the main groups of clay minerals. Their characteristics differing in type and the quantity affect the durability of brick. They are identified by using several analytical methods such as SEM-EDX, XRD analyses, FTIR and chemical methods (Grim, 1968).

A study was done to examine the physical, physicomechanical and mineralogical properties of the bricks of Tahir ile Zühre Mescidi which is a 13^{th} Century Anatolian Seljuk Mescid in Konya (Tunçoku, 1993). The bricks had the bulk densities between 1.38 to 1.47 gr/cm^3, and the porosities between 45 to 48%. The mineralogical composition of the bricks was examined by using XRD. Quartz, feldspar (albite) and iron oxides were the main minerals in their composition. The absence of clay minerals was the evidence of firing temperature. Tunçoku found that the firing temperature was fairly higher to destroy the structure of kaolinite type of clay minerals, but it was below 1000°C (Tunçoku, 1993).

Tiles

The tiles have their front face-glazed, and their back is left unglazed; they have a porous body. They are used for covering the walls for visual preferences and for protecting the masonry from water absorption (Hasol, 2008). Durbin (2005) classified the tiles used in the brick masonry as ‘architectural tiles’. Tiles may include a wide range of ceramic decoration and covering inside and outside the buildings for decorative and functional reasons.

In Seljuk Monuments, tiles were the surface covering materials on the wall together with their mortar. The function of tile mortar, as being a tile bed, was to fix the tiles to the masonry. It was the connection between the tiles and the masonry. Brick masonry was commonly used behind the tile and mortar (Bakırer, 1981).

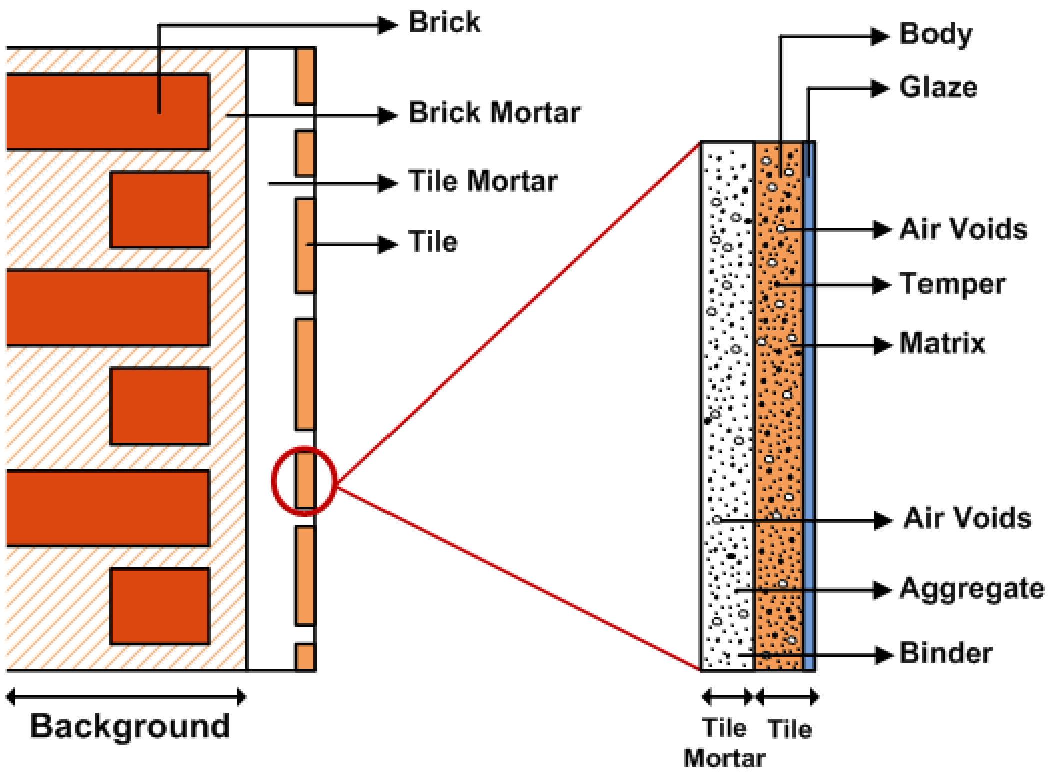


Figure 1.2 A drawing to show the position of tiles on the wall (adapted from Maggetti, 1982, 1994).

The illustration of a tile and its position on the wall is arbitrarily drawn in Figure 1.2. It was adapted from Maggetti (1982, 1994). The tile body consists of air voids or pores, temper minerals and matrix. The pores are formed during the firing process. Some fragments in the body can be temper fragments which are added on purpose (Maggetti, 1982). Those can be sand, crushed flint; shell and limestone fragments and organic materials (e.g. chaff). Their addition to the body can decrease the drying shrinkage and prevent crack formation during drying (Tite, 2008).

Tiles are thinner than the bricks and because of that cannot be placed deep into the wall. They are placed on the jointings and are used on recessed brick units or specific small brick fragments which are probably used for their strengthening (Bakırer, 1981).

Tile units were rectangular/square shaped units or produced by breaking the tile plates to form mosaic tile units. Mosaic tile units were formed by putting mosaic tile pieces with a mortar. (Bakırer, 1981).

Although there were some studies about the technology of tiles, their conservation problems were not defined in detail. Further studies were needed for the conservation problems and methods to prevent further damage to building tiles of Seljuk Period Monuments.

Some **archaeometric studies** on the technology and provenance of tiles and ceramics in Anatolia were carried out on their raw material sources, mineralogical analysis and their glaze characteristics. Alanya Seljuk Palace, Sivas Gök Medrese and Tokat Gök Medrese tiles were analyzed for those purposes.

The study on the tiles of Alanya Seljuk Palace was aimed to analyze their raw material characteristics by using XRD and thin section analyses. 22 glazed ceramic and 19 tile samples, as well as new brick and clay taken from the area, were studied. The mineralogical and petrographical analyses were done by thin section and XRD analyses. The results of thin section analyses showed that the main mineral was angular quartz with coarse grains. Additionally, feldspar was abundantly found. Hematite, micrite, gypsum, biotite, opaque minerals and volcanic and metamorphic rock fragments were determined in the thin sections. It was thought that quartz was artificially added as a temper because of the heterogeneous distribution of mineral grains in the body. Also, a local soil in Alanya was examined with XRD to compare it with the body minerals of tiles. Calcite and dolomite were detected as the main carbonate group minerals in the soil which lower the firing temperature of the body. Thus, the carbonate-rich soil might be added as a temper to the body. Furthermore, opaque coloring materials were determined in the glaze and body of the tiles (Türkmenoğlu et al, 2007).

Another study was done aiming to make a contribution to the conservation of the building tiles by understanding the characteristics of glazed building tile technology and their common features in Seljuk Period Monuments (Sivas Gök Medrese and Tokat Gök Medrese). The analytical data was obtained by using XRD to get the mineralogical composition of body and glaze. In addition, SEM-EDX was used to observe the interaction zones, vitrification properties and elemental composition of glaze and the body of tiles. Besides the physical characteristics of the tile bodies and mortars, their firing temperatures regarding the mineral compositions were determined. The absence of high temperature minerals showed that the firing was low about 800°C. In addition to the properties of tiles, further studies on the deterioration problems needed to be studied in details which were caused by dampness, soluble salts and improper repair materials (Özer et al, 2001, Demirci et al, 1996).

Glazes of the tiles were vitreous surface coverings applied on the tile or ceramic body for decoration and functional purposes. It was applied to the surface of the ceramic body with or without slip. The scanning of the surface by SEM (Scanning Electron Microscopy) and identifying the mineral compositions by XRD were the effective methods to detect the details of glazes such as the adhesion of glaze to surface and their composition (Middleton, 1987). The composition of the glazes and application of glazes on the surface is accepted to be successful if there is no crack or distortion of the body and a uniform distribution of the glaze over the surface without pinholes (Tite et al, 1998).

The first production of glazed objects coincided with the production of glass objects in Mesopotamia around 1500 BC. The glazes were developed together with the development of glass production technology (Tite, 2008).

Composition of glaze and glass are quite similar. Glazes may contain more components for different purposes (Dinsdale, 1986). **Glaze formers** and **modifiers** are the main materials to be used (Hodges, 1964). While glaze formers such as SiO_2 and Al_2O_3 are forming the glass network, modifiers are acting as filler of the holes of glass (Shepard, 1971). Sodium oxide (Na_2O), potassium oxide (K_2O), calcium oxide (CaO), barium oxide (Ba_2O), magnesium oxide (MgO), zinc oxide (ZnO) and alumina etc are the main glaze modifiers. The glaze colorants are used for different colors in different firing temperatures. For example, copper oxide (CuO_2) gives blue or green colors in oxidizing conditions, red or black under reducing conditions depending on the concentrations and modifiers (Hodges, 1964).

The classification of glazes was correlated with the use of lead and tin due to their easier preparation, application and low risk of crazing. Transparent glazes with a high lead content was started to be used in Anatolia during the 1st century B.C. The first lead glazes contained 45-60% PbO, less than 2% Na_2O and K_2O, 2-7 % Al_2O_3 with changing proportions. Lead glazes continued to be used in Byzantine, medieval Europe and Islamic World on the surfaces of pottery and tiles (Tite, 2008). In addition to lead glazes, tin opacified glazes were used by Abbasi Iraq mostly between 8th and 9th centuries (Mason and Tite, 1997).

A study was done to understand the characteristics of some glazed pottery and tile technology of Byzantine and Seljuk Periods in Anatolia. According to the study, the potsherds had lead-based glazes having 11-64% PbO, 30-50% SiO_2, about 10% Al_2O_3. The glazes of Seljuk tiles were alkaline glazes in turquoise monochrome colours having SnO_2 as opacifier. Alkaline monochrome glazes which had violet black colour were also present in Seljuk tiles (Demirci et al, 2004).

Their weathering behavior of glass was characterized by using a *triangular diagram*. The molecular percentages of the constituent oxides were catagorized as *network formers* (SiO_2 etc) having high bond strength, *intermediates* were both for forming and modifying, and *modifiers* which break the silica network to change some properties such as viscosity and durability (Newton and Davison, 1996).

Since, the compositions of Sivas and Tokat Gök Medrese tiles had high silicate contents (Demirci et al, 2004), they can be considered as durable glazes according to Newton and Davison (1996).

Use of Mortars

Mortar is a building material whose main purpose is to attach the masonry units together. It is applied as bedding, jointing, and rendering in brickwork or stonework. It has structural importance to contribute the uniform distribution of loads (Davey, 1961, Holmes and Wintage, 1997). Mortar had the main function of protecting the building against frost and rain. It should never be stronger than its neighbouring materials and must be resilient enough to tolerate minor movements in the masonry (BS 5390: 1976).

For that reason, the mortars need to have different physical and physicomechanical properties depending on the type of material on the structure. Therefore, the type and amount of the raw materials and other additives vary according to the mentioned properties and functions of mortar (Davey, 1961, Tunçoku, 2001).

Binder, aggregate and additives are the main components of the mortar. Mud, lime, gypsum and asphaltic bitumen are often used as binder (Davey, 1961). Aggregates are the natural or artificially obtained materials to be added to the binder to prevent shrinkage and cracks during drying. Natural aggregates are obtained from sand quarries, river or coastal beds. Bricks, tiles, etc are the artificial pozzolanic materials which are ground to desired sizes before use (Davey, 1961). In some studies, aggregates are classified according to their reaction ability with the binder. The studies were done by Jedrzejewska (1960) on 1000 historic Polish mortar samples belonging between the 10^{th} and the 16^{th} centuries. Hydraulic additions such as burned clay, crushed brick and fillers as sand, crushed limestone, crushed fragments of gypsum mortar were the main aggregates used for the mortars (Davey, 1961).

It was known that organic and inorganic additives were added to fasten the carbonation process of lime mortars and improve the physical characteristics of lime or mortars. The historical documents and the scientific studies of mortars were the evidence of using additives in history. Arabic gum, animal glue and fig juice were added as an adhesive. Flour, pig fat, whey, cheese, blood and egg white were used to rapid setting of lime. Barley, urine and animal hair were added to increase the strength etc (Sickels, 1981). The written sources revealed that barley water and elm bark were used as additive in the composition of the mortar of Hagia Sophia (Mango, 1992).

Some additives such as hair, straw or charcoal could be detected by macroscopic or microscopic examination. The others which were not detected macroscopically were identified by specific methods. The characterizations of organic additives were carried out by using wet chemical methods such as gas chromatography (GC) and thermal analysis; differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric methods (TG) and Fourier Transform Infrared Spectroscopy (FTIR) (Middendorf et al, 2005). In addition, some spot tests were used for the identification of proteins and oils. However, they could not be detected due to their small amounts in mortars and their dissociation with bacteria (Middendorf et al, 2005).

A study was done on the bricks and mortars of Tahir ile Zühre Mescidi (Konya) by Tunçoku, 1993. It was proved that the basic properties of bricks with their mortars were very close to each other (Tunçoku, 1993). Another study was done with bricks and stones belonging to twelve Seljuk Monuments to characterize the bricks and brick mortars of Konya. According to the study, the average bulk density was 1.38±0.11 g/cm^3 and the average porosity was 46±7 % for bricks of those twelve Seljuk Monuments. For the same monuments, the average bulk density was 1.5±0.15 g/cm^3 and the average porosity was 41± 7% for brick masonry mortars. Moduli of elasticity of Seljuk Period building mortars had average value of 1555.2 ±704 MPa (Tunçoku, 2001).

The properties of mortars were depended on the materials used in combination with them. For example, the brick masonry mortar was lighter and more porous than that of the stone masonry mortar. In addition, bricks and mortars of brick masonry formed light, porous and homogenous upper structures acting consistently against external conditions (Tunçoku, 2001).

The same principle was also valid for tiles and the mortars. Although they had no structural features on the surface of the building, they were expected to have similar physical and physicomechanical properties. While the mortar, bricks and tile bodies had different compositions, mortars were prepared to have similar physical and physicomechanical properties by the addition to suitable types of binder, aggregates and additives.

The use of **gypsum mortar** was quite ancient. It was deliberately produced binding material which was used from the beginning of the 3rd century B.C. It was used as mortar and plaster for example in the construction of Egyptian pyramids between the stone blocks and as a plaster (Livingston et al, 1991; Davey, 1961, Torraca, 1982). Natural gypsum quarries were used to prepare gypsum binder. The gypsum binder was prepared either by heating the gypsum rock to form hemihydrates or by more heating to form anhydrite.

Gypsum ($CaSO_4.2H_2O$) is found in nature as gypsum rocks. It was taken from gypsum quarries and broken to gypsum lumps. The lumps were burnt in a kiln between 130 and 170°C for about three hours to form plaster of Paris, bassanite or hemihydrates ($CaSO_4.{}^1/_2H_2O$). 400°C was needed to get mineral anhydride ($CaSO_4$) from gypsum (Davey, 1961, Torraca, 1982).

Pure gypsum has relatively high solubility being 2 g/l at 20°C (Lange, 1952). Gypsum was used in arid areas because of its relative solubility. It was also used in wet climates by lowering the solubility with some additives in preparation of gypsum mortars and plasters. The use of gypsum had advantages such as rapid setting time, higher strength; visual appearance and low manufacture costs (Livingston et al, 1991).

During the preparation of gypsum mortar, it was not needed to use aggregates (Livingston et al, 1991), because the setting time of plaster of Paris was very short to form hard gypsum after mixing with water. In addition, some water was lost and the gypsum crystals expand during the setting reaction which made the fillers unnecessary against contraction and crack formations (Torraca, 1982). For instance the studies showed that the gypsum mortars of Egyptian monuments had the ratio of 0 to 0, 27 sand to gypsum (Livingston et al, 1991).

The setting time of gypsum mortars was controlled by some additives. While gypsum dust was used for accelerating, organic materials such as glue or starch were used for retarding the setting time of gypsum based materials (Torraca, 1982).

Some precautions must be considered while restoring gypsum based mortars. For instance the use of cement based mortars for restoration causes the reaction between gypsum and cement, producing ettringite ($3CaO.Al_2O_3.3CaSO_4.31H_2O$) (Woods, 1968). Ettringite is harmful due to its large volume of water it contains. The higher volume was caused the destructive expansion of material forming spalls and cracks (Sabboni et al, 2000).

Today, two types of hemihydrates from gypsum rock are produced by changing the burning conditions. α-Hemihydrate (crystalline hemihydrate) is produced by heating in autoclave with high pressure and water vapor. Their product is well crystallized, has lower porosity and reacts more slowly with water. β-Hemihydrate (microporous hemihydrate) is produced by heating in dry atmosphere. The product which has smaller crystals and larger pore dimensions reacts more rapidly with water (Torraca, 1982).

1.4.1 Decay Problems of Tiles and Bricks

In historic structures, tiles and bricks were used together with tile mortar to attach them to the masonry. The durability of tiles and bricks was due to their durability towards cyclic changes of humidity, temperature and other environmental factors and compatibility with their mortar. However, the compatibility of the materials could adversely change in time. Wrong restoration interventions and the environmental conditions such as air pollution might cause their deterioration. Loss of tiles as a result of salt crystallization was one of the most important decay factors formed in many historic structures.

The deterioration of bricks and tiles could be physical such as their disaggregation by frost and salt weathering as well as some chemical deterioration due to the interaction with polluted air (Lopez-Arce and Garcia Guinea, 2005). Although the surface of tiles was covered with glaze, the salt crystals were deposited under the glaze causing the physical and chemical damages to the material (Borges et al, 1997).

1.4.2 Salt Decay Problem of Porous Building Materials

It is crucial to understand the weathering processes of porous building materials by salt crystallization. The damage process of salt crystallization and the origins of soluble salts are discussed here.

Salt crystallization was an important decay factor for porous materials (Arnold, 1981, Caner-Saltık et al, 1998; Pel et al, 2004; Lubelli et al, 2004).

Salt is accepted to be a deteriorating agent when it is combined with water or moisture and moved through the porous body (Snethlage and Wendler, 1997). Although lower concentrations might cause damage in time, it is accepted that it give harm to the porous body while salt concentration is higher than 1% in the material e.g. brick masonry which depend on the properties of the materials (Friese, 1991). Salt moves through the wall and on the surface with rising damp as an aqueous salt solution. The ions are transported by water as dilute aqueous solution. Its concentration is increased by increasing the evaporation of the solvent. The solution becomes supersaturated with the movement and evaporation of water (Arnold, 1984). When the solution becomes supersaturated, crystallization occurs in the upper section of rising damp on or beneath the surface (Arnold, 1988; Lubelli et al, 2004).

The salt solution goes along with the empty spaces such as capillaries and pores of the material. The salt solution is accumulated and crystallized in the pores. Thus, the crystallizing salts expand in the pores by exerting pressure on the walls of the pore, which cause loss of adhesion in the material (Franke et al, 1998). The crystallization-recrystallization cycles of salts in the pores increase the deterioration which is due to the fluctuation of relative humidity in the environment (Arnold, 1988; Lubelli et al, 2004).

Figure 1.3 shows a schematical representation of salt attack in a building wall.

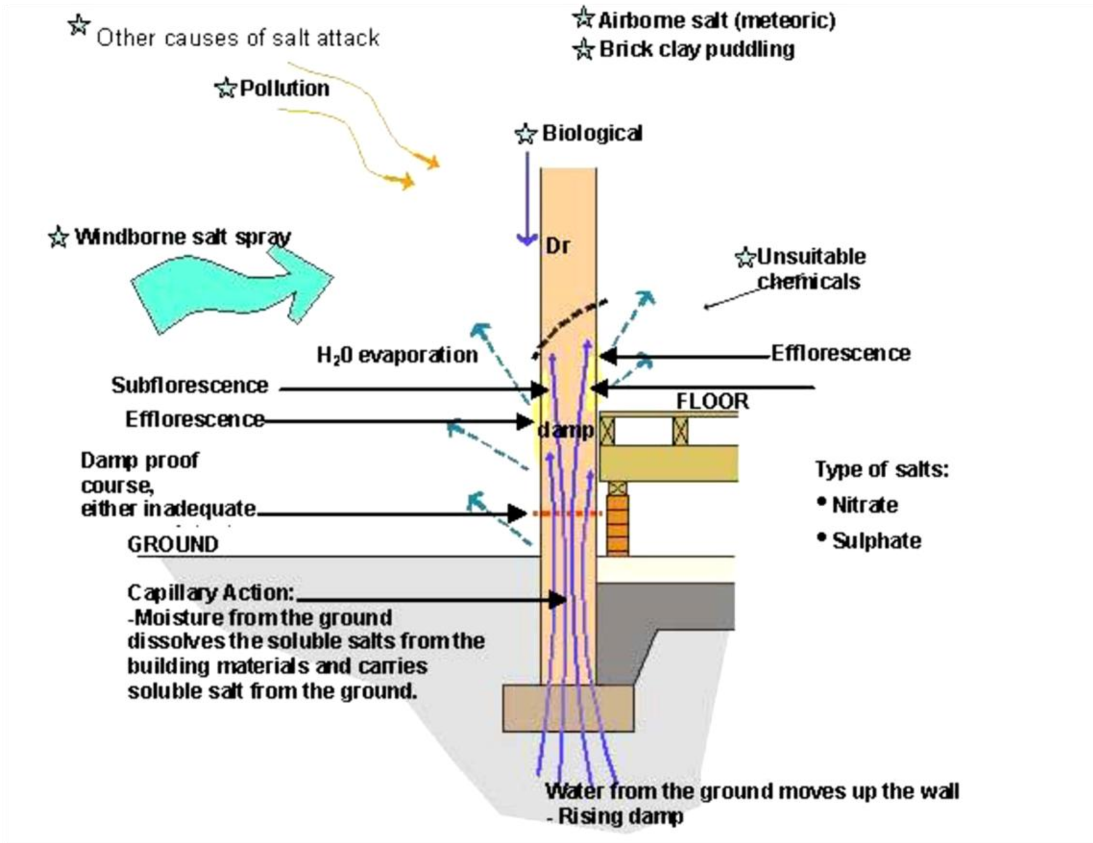


Figure 1.3 Schematic representation of salt attack in a building wall (Ahmad et al, 2010).

The thermodynamic equilibrium of salt solution is to be considered to understand the damage mechanisms by salt crystallization. For a supersaturated salt solution, free energy is released from the system causing the formation of crystals as a spontaneous process. The energy released from the system is sufficient to cause mechanical failure by expansion (Lewin, 1989).

The terminology of salt crystallization changes according to its accumulation zone in the material. The crystallization of salts within the pores of porous building materials is called “florescence”. If crystallization is formed on the external surface of the material, it would be called “efflorescence”. Also, if the crystallization is formed within the pores, it would be called “Cryptoflorescence” or “Subflorescence” which is mainly formed from a millimeter to a few millimeters beneath the surface. They frequently occur together as shown in Figure 1.3 and Figure 1.4 (Schaffer, 1972; Rodriguez-Navarro and Doehne, 1999).

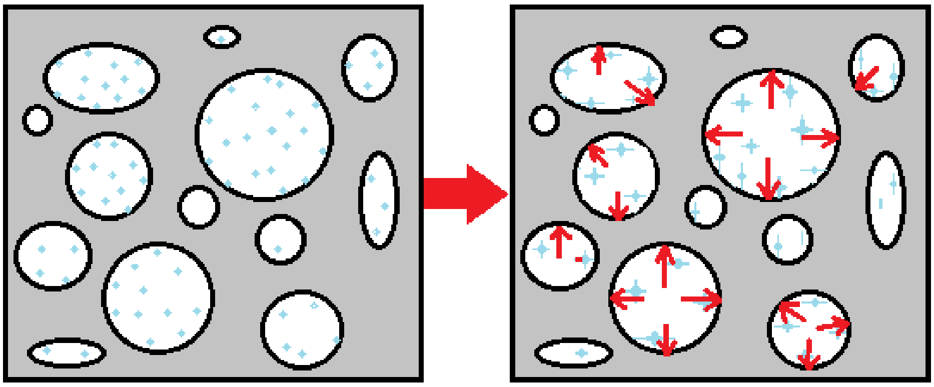


Figure 1.4 The crystallization of salt solution in the pores causing pressure to the walls of pores: cryptoflorescence or subflorescence (before and after crystallization)

Origins and Reactions of Salt Solutions

The origin of soluble salt problem must be defined in relation with the environment, location and history of the building (Freedland, 1999).

The salts could be originated from the original building materials or the external sources. Stones of the building might be a source of salt in the building (Arnold, 1988). Soluble salts present in the material may be derived from the external sources. The external sources are from the incompatible materials for cleaning and preservation, ground water, polluted atmosphere and some unknown sources (Schaffer, 1972).

The use of incompatible materials next to each other may be a source of salt such as Portland cement or waterglass. They supply alkaline ions, which convert alkaline earth sulphate, nitrate and chloride salts to alkaline salts. Alkaline salts are more harmful than the others because of their higher crystallization abilities in a humid atmosphere (Arnold and Zehnder, 1989). They could react either with materials or the original building salts. The reaction of alkaline salts in ancient walls is given in a general equation (1.1) below (Arnold, 1981).

(1.1)

$$\begin{Bmatrix} \mathbf{Na^+} & \mathbf{K^+} \\ \mathbf{OH^-} & \mathbf{CO_3^{2-}} \end{Bmatrix} + \begin{Bmatrix} \mathbf{Mg^{2+}} & \mathbf{Ca^{2+}} & \\ \mathbf{SO_4^{2+}} & \mathbf{Cl^-} & \mathbf{NO_3^-} \end{Bmatrix} \rightarrow \left(\begin{Bmatrix} \mathbf{Ca} \\ \mathbf{Mg} \end{Bmatrix} \mathbf{CO_3} \right) + \left(\begin{matrix} \mathbf{Na} \\ \mathbf{K} \end{matrix} \right\} \begin{Bmatrix} \mathbf{SO_4} \\ \mathbf{Cl} \\ \mathbf{NO_3} \end{Bmatrix} \Bigg)$$

According to the equation (1.1), the salts of alkali sulfates, chlorides and nitrates are formed. They are the most frequently efflorescing salts on the wall because the RH_{eq} of alkali nitrates are higher than earth alkaline nitrates which mean that they precipitate more frequently (Arnold, 1981).

Ground water from the soil may contain some soluble salts mainly such as sodium chlorides, sodium sulfates, and potassium nitrates which may contribute to the formation of florescence (Schaffer, 1972). In addition, the polluted atmosphere cause the formation of salts by reacting with building materials (Schaffer, 1972; Arnold and Zehnder, 1989).

1.4.3 The Effects of Salt Crystallization in the Building Material

Examination of damage due to salt crystallization and assessment of the degree of damage was important for the conservation of historic brick structures. The florescence resulted in different damage types on the brick or stone. The deterioration forms, common for all the porous materials were flaking (contour scaling), powdering (sanding) etc. (Snethlage and Wender, 1997, Caner-Saltık et al, 1998).

Weathering forms of a brick may also be related to its production technique e.q. bricks produced by extrusion should be more susceptible to **flaking** and spalling due to the concentric layers of clay minerals whereas hand-molded bricks are more affected by **sanding off** (Franke et al, 1998).

For parts of the building that stay wet over a long period or exposed to frequent rainfall, **flaking off** should predominate. Moreover after the experiments, Franke (1994) stated that salt containing bricks had decreased vapor diffusion transport due to water remaining longer in bricks.

1.4.4 Conditions that Affect Salt Damage

Air humidity, pore characteristics of bricks and tile bodies, calcite contents of clays and type of salts are the main factors affecting salt damage.

1.4.4.1 Air Humidity

The crystallization of salt phases is controlled by the air humidity (Arnold, 1988). In low relative humidity conditions, salt is in crystalline form. As relative humidity increases, it becomes a saturated solution by absorbing water molecules from the air. Further absorbing water makes the solution diluted. By lowering of relative humidity, water evaporates from the solution to the air. The salt crystallizes at the lower relative humidities than its equilibrium relative humidity at a given temperature (Steiger and Zeunert, 1996). The equilibrium between the solution and the relative air humidity is given by the equation **(1.2)** below:

$$(P_{H2O}^{S}/P_{H2O}^{W}*)100 = RH_{eq} \qquad (1.2)$$

P_{H2O}^{S} = Water vapor pressure of saturated salt solution

P_{H2O}^{W} = Water vapor pressure of saturated air

RH_{eq} = Relative humidity in equilibrium with the saturated solution.

For the supersaturated salt solution and subsequent precipitation, the relative humidity of ambient air (RH) must become lower than the equilibrium relative humidity (RHeq): $RH \leq RH_{eq}$ (Arnold, 1988).

The crystallization of salt can only occur when the ambient relative humidity (RH) becomes lower than the saturated equilibrium relative humidity of salt solution. Reversely, salt dissolves when RH rise above RH_{eq} (Arnold, 1981). Table 2.1 includes the equilibrium relative humidity of some pure salt solutions at different temperatures.

Table 1.1 Some salts with their equilibrium relative humidities

Salts	**Formula**	**RH_{eq} (%)**	**T (°C)**
Gypsum	$CaSO_4.2H_2O$	99.6***	20
Halite	NaCl	75.3*	25
Natron	$Na_2CO_{3.}10H_2O$	92*	18.5
Natrite	Na_2CO_3	91.6**	20
Nitratine	$NaNO_3$	73.9*	25
Niter	KNO_3	92.5*	25
Thenardite	Na_2SO_4	81*	25
Sylvite	KCl	56-63****	20

*(Arnold, 1981), ** (Apelblat and Manzurola, 2003), *** (Zehnder, 1993),
**** (Lo´pez-Arce et al, 2011)

In reality, the salt precipitations are the mixture of different salts each having different equilibrium relative humidity. It is complicated to predict the equilibrium relative humidities of mixed solutions. The efflorescence of mixed solutions is observed in lower relative humidity values than the pure ones (Arnold and Zehnder, 1989).

It is emphasized that the changes of relative humidity of the ambient atmosphere cause the crystallization cycles (Caner-Saltık, Schumann, Franke, 1998; Steiger and Zeunert, 1996). For that reason, microclimatic conditions must be controlled to prevent salt crystllization. The relative humidity of the environment must be kept constant to avoid wetting-drying cycles, which is possible only for indoor objects. For outdoor objects salt crystallization cycles can not be stopped unless they are cleaned from salts (Pel et al, 2004).

1.4.4.2 Pore characteristics of bricks and tile bodies

Durability of porous building material is affected by its pore characteristics; **porosity**, **pore size distribution** and **pore shapes** (Benavente, Linares-Fernandez, Cultrone, Sebastian, 2006). The pores being the air voids, capillaries are the empty spaces of porous building material which might be naturally present and formed as a result of decay processes. Thus, the distribution of pore characteristics might be uniform or locally formed (Jedrzejewska, 1970).

The pores in bricks are evolved by the mineralogical and textural changes of clay minerals during the firing process. The studies of Benevante et al (2006) showed that increasing temperature lead to the formation of more homogenous and resistant bricks. During firing, larger pores formed, and the smaller ones disappeared due to the vitrification process. Thus, increasing firing temperature resulted in the lowering of porosity; pore radius was increased, which meant more resistance to salt attacks. Benevante et al (2006) studied the optimum firing temperature of the hand-molded bricks having known physical and chemical properties. They found that the optimum firing temperature was 1000°C with regard to the vitrification process. It was economically necessary to produce resistant bricks to salt attack.

For the removal of salt in materials, water has to enter the open pores to dissolve the salt crystals (Jedrzejewska, 1970). For that reason, open pores of bricks are the key factor because the salt solution can only reach the open pores and salt precipitation occurs there.

Studies showed that crystallization of salt took place initially in the larger pores (Franke et al, 1998). From the field studies of Zehnder and Arnold (1989), it was observed that salt was mainly crystallizing in pores with the dimension between 1-10μm. If they were filled with salt, the remaining salt crystallized in smaller ones. The smaller pore radius ranged between 1-5 μm where crystallization occured (Franke et al, 1998).

Pore characteristics were changed by salt crystallization pressures due to the increase in the finer pores and total porosity of the samples. Salt crystallization caused an increase in water absorption and water vapor sorption properties (Caner-Saltık et al, 1998).

According to Rossi-Manaresi and Tucci (1989), the theoretical calculation of the salt crystallization pressure was done in relation to the pore structure. The equation was as given below:

(1.3)

$$\mathbf{P = 2\sigma\left(\frac{1}{r} - \frac{1}{R}\right)}$$

Where:

P : Crystallization pressure (atm)

σ : Interfacial tension of salt solution (80dynes/cm)

r and R : radius of small and coarser pores

The equation showed that the percentage of smaller pores were the determining factor of the crystallization pressure. It was stated that the radius of small pores were less than 1 micron (Rossi-Manaresi and Tucci, 1989), but the effect of the concentration of salt crystals was disregarded in the equation.

It was necessary to better determine the **pore size distribution** of the samples to identify the effect of salt crystallization. There were some methods such as mercury porosimetry, water suction, analysis with Scanning Electron Microscopy (SEM) and image analysis. Mercury porosimetry was used by repeated intrusion and extrusion of mercury into the pores. The breakthrough of the small pores might result in the measurement errors. Thus, mercury porosimetry might not be an effective method for all the cases (Caner-Saltık et al, 1998) especially for the deteriorated historic materials. The suction and moisture absorption method was based on the pressure of water in the pores of the material. A logarithmic suction scale was drawn with a 'suction plate method'. It could be used to make a pore distribution diagram. It was used also for the identification and provenance of marbles by De Castro (1988). The porosity characteristic was also done also by image analysis with the streomicroscope and SEM (Scanning Electron Microscope) (Maria, 2010).

1.4.5 Types and Sources of Salts

The presence of florescence in building materials was accepted to result in their physical and chemical deterioration (Teutonico, 1988).

Potassium and **sodium carbonate minerals** were the products of modern alkaline building materials such as Portland cement and water glass. Their alkali hydroxides were affected from carbonic and sulfuric acids to produce carbonates and sulfates.Examples were kalicinite ($KHCO_3$), natron ($Na_2CO_3.10H_2O$) and trona ($Na_3H(CO_3)_2.2H_2O$) (Arnold, 1981).

Sulfate minerals commonly found as hydrated form of calcium sulfate; gypsum ($CaSO_4.2H_2O$) and less commonly magnesium sulfate ($MgSO_4$). Various sulfate sources were found either in the environment or in the original material, agricultural areas, microbiological activities, sea water (containing little amount of sulfates), and atmospheric pollution could be the source of sulfur dioxide (SO_2) for salt formation, or they were direct salt sources (Teutonico, 1988).

Chloride minerals were more frequently observed in coastal regions (Arnold, 1981). They also originated from the impurities in the materials coming from sea such as sand for mortars and plasters. In addition, they were the result of some industrial activities. The presence of gaseous HCl in the air was evidence of pit-coal burning (Teutonico, 1988). Halite (NaCl) and sylvite (KCl) were examples of common chloride salts. Ca and Mg chlorides were not detected easily due to their high hygroscopicity (Arnold, 1981).

Nitrite and **nitrate** minerals were the decomposition products of organic materials containing nitrogen. The initial form was nitrite which then oxidized to form nitrate which was more commonly seen than the others. The earth in agricultural areas and atmospheric pollution were the principal nitrate sources. Combustion of hydrocarbons produced sulfur dioxides, organic molecules and nitrogen oxides. As a result of complex reactions, nitric acid and calcium carbonate minerals form calcium nitrates (Teutonico, 1988). Niter (KNO_3) and nitratine ($NaNO_3$) were the examples of nitrite salts.

Ca and **Mg carbonate** deposits on stone and brick materials might be due to dissolution and recrystallization of the production of different salts or components of the building materials such as limestone, dolomite and mortar (Arnold, 1981). Although $CaCO_3$ is insoluble in water, it could be dissolved to form bicarbonates in slight acidic environment depending on the concentration of CO_2 (Teutonico, 1988).

Salt Decay as Gypsum Formation

Gypsum has low solubility, its crystallization and the damage process is rather slow. (Arnold, 1998). According to Zehnder (1993), the formation of gypsum crystals was seen in the drier upper parts of the walls as well as the lower parts affected by rising damp. It was formed especially:

- Gypsum was found as black crust on the surface of calcareous building materials affected from polluted atmosphere by the reaction with sulfuric depositions.
- It was also found at the interior side of the walls where water reached. In that case, it was generated from the building materials such as stone mortar or repair materials.
- Ground water was also the additional gypsum source.

The formation of a gypsum crust proceeds as follows: some pollutants such as SO_2, CO_2 and NO_x from the air cause damage to acid sensitive minerals in bricks such as calcite or feldspar in humid air. Ca^{2+} from the minerals precipitates with SO_4^{2-} of sulfuric acid to form gypsum. Thus, damage starts with the surface of the brick. Flake and scale formation, powdering can be observed in bricks due to salt damage (Franke et al, 1998). Ground waters, building materials and air could be the source of sulphates to form gypsum (Arnold, 1998).

Gypsum was evaluated as a salt rather than an agent causing the formation of different salts. However, the studies on the plasters and mortars of Saray Bath in Edirne proved the formation of a different salt by gypsum. The analyses were done on the deteriorated lime-based plaster samples which had brick fragments as aggregate and gypsum as additive for the early strength of materials. The reaction of metakaolin in brick powders and lime resulted in the formation of calcium aluminum hydrates and calcium silicate hydrates which was called as ‘pozzolanic reaction products’. The products might then react with gypsum at high humidity conditions. The resulting salt was called ‘ettringite’. It had higher expansion forces due to its water content. The equations (1.4) and (1.5) were given below (Böke and Akkurt, 2003):

(1.4)

$Al_2O_3.2SiO_2+7Ca(OH)_2+19H_2O \rightarrow 4CaO.Al_2O_3.19H_2O+3CaO.2SiO_2.7H_2O$
(metakaolin)(hydrated lime) *(CAH)*
(1.5)

$CaO.Al_2O_3.19H_2O + 2CaSO_4.2H_2O +11H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.34H_2O$
(CAH) *(gypsum)* *(ettringite)*

CAH: $CaO.Al_2O_3.19H_2O$ (Calcium Aluminum Hydrate)

CSH: $CaO.2SiO_2.7H_2O$ (Calcium Silicate Hydrate)

The other type of salt was thaumasite, which was found in gypsum lime mortars and plasters in masonry of historic buildings (Tesch and Middendorf, 2006). It was a salt composed of calcareous and siliceous components with gypsum ($CaCO_3.CaSiO_3.CaSO_4.15H_2O$) (Van Hees, Wijffels and van der Klugt, 2003). The differentiation with X-ray diffraction (XRD) was difficult due to the similarities of the crystal structures of thaumasite with ettringite (Tesch and Middendorf, 2006).

The formation of thaumasite depended on the presence of sulphates, silicates, carbonates, calcium and water under low temperature (0-15°C), high humidity conditions and pH lower than 10.5. It caused the swelling and decrease of the soundness in mortar (Tesch and Middendorf, 2006).

For those reasons, the gypsum containing materials must be preserved to prevent ettringite and thaumasite formation at high moisture (Böke and Akkurt, 2003; Van Hees et al, 2003).

The effect of gypsum crystals on the drying behavior and capillary suction of bricks were studied by Franke and Graubau (1998). In the experiments, saturated magnesium sulfate and gypsum solutions were used. The bricks were exposed to the salt solution in their one side. Evaporation rates, drying behaviors and their capillary suction differences were measured by gravimetry. The results showed that an increase of salt content decreased the drying behavior and the water vapor transport of the bricks. More specifically, gypsum containing bricks had significantly lower drying and vapor transport rates than the same gypsum-free bricks. It was called as the “pore blocking effect of gypsum”.

1.4.6 Other factors causing damage

The characteristics of drying affect the damage to the bricks. A slower drying rate causes the water to stay longer in brick which results in the frost damage. Higher moisture content may also increase the sorption of acid pollution gases, which can cause further material damage (Franke et al, 1998).

1.4.7 Methods of Detecting Salts

Different methods are used to identify the salt minerals. Spot tests were used to detect anions in the salt solutions as PO_4^{-2}, SO_4^{2-}, Cl^-, NO^{2-}, NO_3^{2-} and CO_3^{2-}. The crystalline minerals of efflorescence could be identified by XRD. Additional methods were also used as optical microscopy and SEM (Arnold, 1984).

1.5 Control of Salt Damage

The salts on the wall cause severe damage as mentioned above. Studies have shown that several treatments on the salty surface had limited effects. Also, the damaging effects of salts have increased with some conservation treatments (Binda, Baronio and Ferrieri, 1996). Therefore, the extraction of salts from the historic materials was of prime importance.

For the extraction of soluble salts, first the sources of them must be detected, and their effects must be minimized by preventing water penetration (Schaffer, 1972). The next step is to study on the best method for the desalination of masonry.

1.5.1 The Methods of Extracting Salt from the Porous Building Material

Salt crystallization was proved to be a common deterioration problem for the porous building materials, since cyclic crystallization at the surface and interiors damaged the material. It was necessary to prevent rising damp and extract the soluble salts from the porous material as mortar, brick and stone (Schaffer, 1972; Friese, 1988). It was more difficult to extract salts from the in-situ materials than the small objects. In addition, some materials were adversely affected from water such as pigments, binding media and their sensitive nature (Pel, Sawdy, Voronina, 2010).

The type of salt had little influence on the extraction methods. The important point was to investigate the distribution and amount of soluble salts on the material. Salts might be near the surface or distributed in the material. It was crucial to select the best method for desalination (Jedrzejewska, 1970). During and after the application of the selected method, the physical properties such as color and mechanical properties of the materials should not be adversely affected (Skibinski, 1985).

Some methods were studied to extract soluble salts such as desalination by diffusion of salt ions, desalination by advection-based methods, vacuum fluid impregnation technique and electrochemical desalination. Electrochemical desalination was not studied by other researchers and its efficiency seemed to be restricted to some local applications on the masonry.

The methods are briefly described below.

1.5.1.1 Desalination by Diffusion of Salt Ions

Desalination was the transportation of salts from the porous material to another media (Friese, 1991).

The techniques of desalination by diffusion of salt ions were applied by using different methods. Desalination by wet-poultices or complete immersion of materials to water baths was the main types.

The principle of the technique based on the movement of salt ions from the high concentration to the lower concentrations. Wet poultices having water retention and low capillarity were applied on the surface. The penetrating water from the poultice dissolved the salts creating a solution with higher salt concentration than the poultice. Thus, the ions were moving through the poultice by diffusion in wet media. Commonly clay and cellulose based wet poultices were used in architectural conservation but, the effectiveness of the technique was still under discussion. Blotting papers and cellulose powder poultices were also used in the literature but, they were not efficient on the deeper parts of substrate and had a risk of moving salts on the deeper parts (Friese, 1991; Vergés-Belmin and Siedel, 2005).

The other technique was the complete immersion of materials to the water. The body contaminated with salt solution was totally embedded in distilled water. The salt solution moved from high to low concentration up to equilibrium concentration (Friese, 1991). For the desalination, the tiles in the deionized water were monitored with conductometric measurements for about one month depending on their size. The qualitative and quantitative analysis of extracted soluble salts were reported with ion chromatography (Borges et al, 1997). The technique was not a way of complete desalination.

The diffusion method had low efficiency (Skibinski, 1985). A simulation was done with a porous masonry wall to estimate the duration of desalination. The results showed that while it was needed 10 days for the 80% desalination of first 20mm, 250 days were needed for the nearly complete desalination of sample with 100 mm which was a slow process (Pel et al, 2010).

Another method to extract the soluble salts from the porous body was by pressing water as a driving force, which based on “convective transportation”. The complete desalination was claimed to be achieved by using that technique (Friese, 1991). Although the complete desalination by diffusion of salt ions might be possible, it was slow. Thus a faster desalination process was required. In addition, it was difficult to apply for in-situ materials on the building such as architectural surfaces (Pel et al, 2010).

1.5.1.2 Desalination by Advection-Based Methods

It was the new intervention technique for desalination of masonry. Desalination by advection based on the extraction of salts by the moisture flow. The method was used for the in-situ materials by using poultices on the wall (Pel et al, 2010). The poultices were made of different hydrophilic moistened materials for advection to apply on the salty surface (Vergés-Belmin and Siedel, 2005).

Wet poultices were applied to the surface for the penetration of water through the substrate. During the wet application, the salts were migrating in the opposite direction of the poultice. It was waited till the drying of poultice. During the evaporation of water from the poultices, the salts migrated through the poultice (Pel et al, 2010).

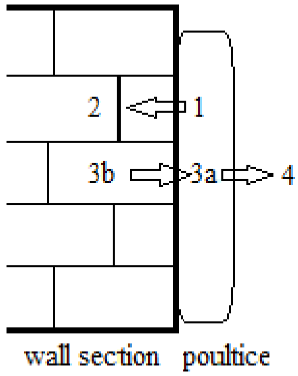


Figure 1.5 Schematic representation of desalination with poultices by advection based method

The water would carry dissolved ions from the substrate to poultice to eliminate salts from the substrate. The treatment worked in two steps: wetting and extraction phases. In the first step, water moved from the poultice to the porous substrate and the salts dissolved with water in substrate (1→2 in Figure 1.5). The second step was the movement of salty solution towards the poultice (3b→3a in Figure 1.5) from the poultice through the evaporation of water (3a→4 in Figure 1.5). So the soluble salts moved away from the substrate (Pel et al, 2010).

The efficiency of the method based on some variables such as the solubility and the distribution of salts in the material. In each case, the variables also the efficiency of extraction were changing (Pel et al, 2010).

The movement of salty solution was dependent on the concentration differences and capillarity of pores of poultice and the salty material. The moisture flow was affected from the relative pore characteristics of poultice and substrate. The suction forces of poultices had to be higher than the substrate for the flow of aqueous solution. So the ions could migrate from substrate through the poultice. For that reason, the relative pore size distributions were the main parameters for the advection of ions (Bourgés, Vergés-Belmin, 2008).

While advection of water performed relatively through the macropores, micropores had relatively lower contribution of flow due to their smaller volume. Furthermore, the poultice had to have smaller pore sizes than that of the main pores of substrate because the migration of water started from the bigger pores through the smaller ones. Thus, the open pores of the poultice had to be smaller than the open pores of the substrate to eliminate their salts. The initial drying of the poultice resulted in the flow of water from the substrate towards the poultice together with the ion transport by advection (Pel et al, 2010).

The difference between diffusion and advection is that, diffusion based on the ion transport in liquid media and advection based on the transport of salt solution by liquid through the drying poultice which was faster than diffusion and was more suitable for immovable objects. In order to get good result, the relative porosity of poultice must be optimized (Lubelli et al, 2010).

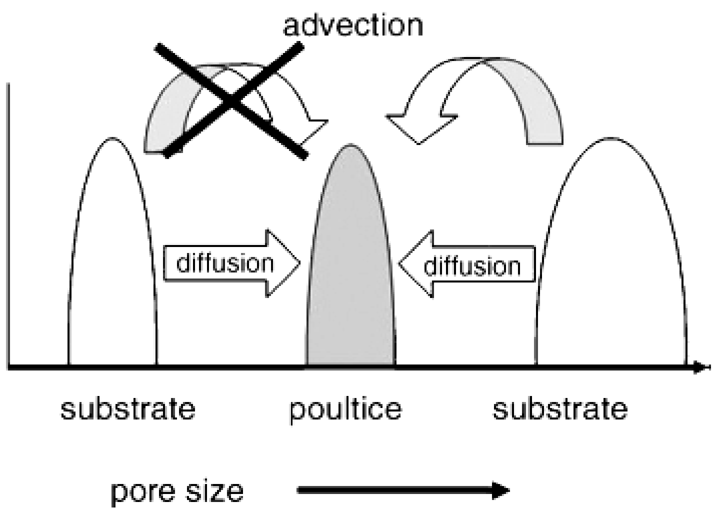


Figure 1.6 Schematic representation of the relation of diffusion and advection with pore sizes of substrate and poultice (Pel et al, 2010).

As shown in Figure 1.6 that aqueous ions migrated from the substrate through the poultice having lower and higher pore sizes with diffusion. Thus, the diffusion was not dependent on the pore sizes. In advection, the aqueous ions migrated from the bigger pore sizes to the lower ones. If the relative pore sizes of poultice was smaller than substrate, the aqueous ions migrated only from the substrate to poultice which had smaller pore size distributions (Pel et al, 2010).

1.5.1.2.1 Identifying the Suitable Type of Poultices

Studies were conducted to prove the relation of pore size distribution with desalination by advection of substrate and poultice. Recent analyses were done by Lubelli et al, 2010 and Bourgés and Verges-Belmin, 2011. As mentioned before, the optimum salt extraction was done by advection which was faster than diffusion and suitable for immovable materials. For the optimization of salt extraction, the pores of poultice must be smaller than the pores of substrate. For that reason, the different poultices were prepared to have different pore sizes. Sand, cellulose, kaolin and bentonite were used in different proportions in the conservation practices. Their qualifications were described in detail. The results revealed their different pore characteristics.

The pore size distributions of some poultices were designed for a substrate. They were prepared under standard conditions and, their effectiveness was evaluated in detail. Bourgés and Verges-Belmin conducted a study to compare the pore size distributions of some poultices with the substrate (2011) (Figure 1.7). Different poultices were prepared with pure cellulose powder mixture (BC1000/BW40), kaolin-sand and bentonite-salt mixtures and a mixture of cellulose, kaolin and sand poultices.

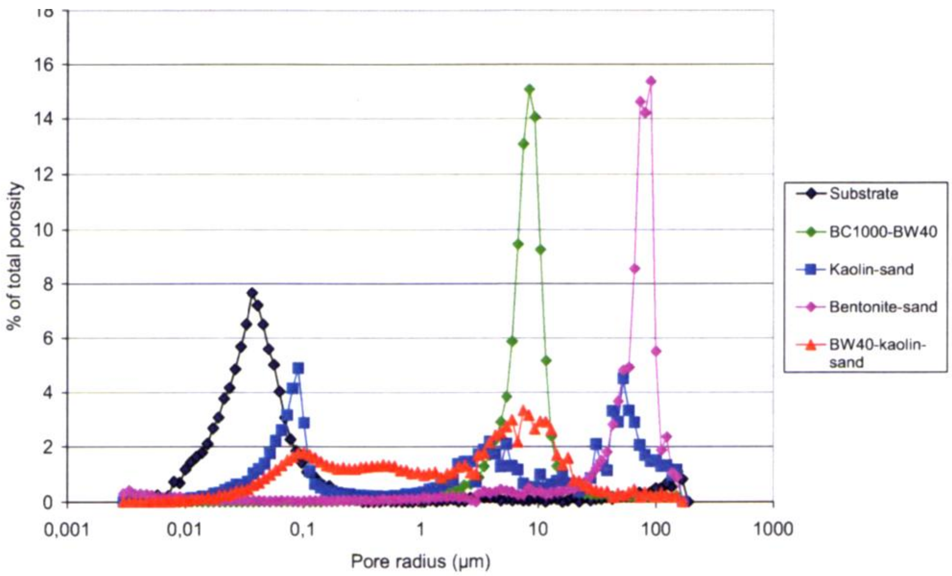


Figure 1.7 The comparison of pore size distributions of poultices which were prepared by different hydrophilic materials and substrate (Bourgés et al, 2011)

According to the pore size distribution graphs (Figure 1.7), the writers stated that the pore size distributions of the two poultices kaolin-sand and BW40-kaolin-sand were overlapped by the pores of the substrate.

In the studies of Lubelli et al (2011), some results were found for the cellulose, bentonite, kaolin and sand which were common for conservation practices. Cellulose was not effective for pores smaller than 15µm for advection. Bentonite/sand mixtures had large pores to prevent effective advection but, while cellulose was added, it might be effective for pores larger than 1-2 µm. Kaolin had 0.3 µm of interstitial porosity. The preparation of kaolin/sand and cellulose/kaolin/sand in different proportions having a large range of pore sizes were the effective methods. Although kaolin had limited shrinkage and effective for desalination, it caused whitish deposits on the surface after desalination, which could be solved or alternative materials could be examined. Sand used was fine(0.08–0.5 mm) and coarse (0.5–1 mm) in the preparation of the poultices (Lubelli et al, 2010).

Figure 1.8 showed some graphs of some selected poultices having smallest pore size distributions (Lubelli et al, 2010). The first graph on the left belong to the kaolin-sand (1:3 by mass) poultice. Sand had coarse grains (0.5-1mm). Its water content was at 0.22 (weight water/weight dry poultice), and its peaks were on 0.2µm and 20µm. The second graph in the middle had two peaks at 0.3µm and 5µm. It was a mixture of kaolin/sand (1:3 by mass) prepared by sand with fine grains (0.08mm-0.5mm) and water content at 0.22. The last graph on the right had a peak at 25µm. It was made of bentonite/sand (1:3 by mass) prepared by sand with fine grains (0.08mm-0.5mm) and water content at 0.22.

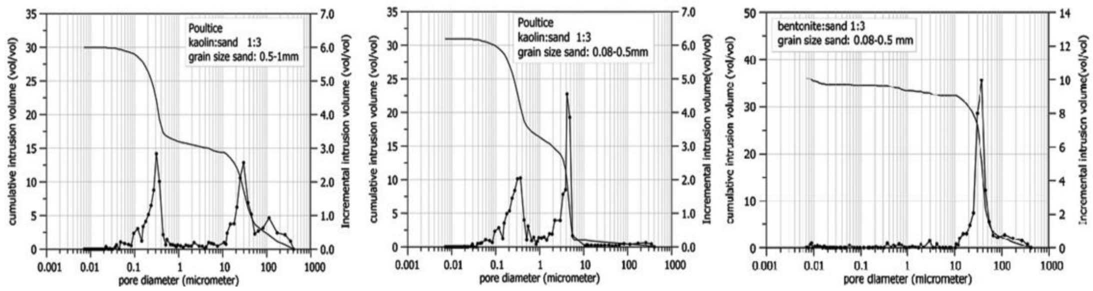


Figure 1.8 The pore size distribution graphs of some selected poultices having smallest pore size distributions (Lubelli et al, 2010)

The expected properties of the prepared mortar must be easy to prepare, apply and have a strong adhesion to substrate. Their workability and consistencies were measured numerically by several experiments by Bourgés and Vergés-Belmin (2011). The workability was conducted by flow tests. It consisted of applying a fifteen successive shocks on the flow table. The poultice spread vertically on the table. Its width was measured before and after the application (Flow; E %). The consistency of material was conducted by putting a cone on the freshly moulded poultice. The cone was penetrating through the poultice by its own weight. The height of the cone was measured as P (penetration depth, mm) of the poultice. Another main experiment was the determination of adhesion with the poultice and substrate. Although the experiment was not standardized, it was done with a flow table.

A brick having determined porosity and capillary adhesion properties was attached on the flow table. The poultice was applied on the brick, and successive shocks of the table causes them to flow on the brick. The evaluation was done to measure the remaining part of the poultice on the substrate (Bourgés, Vergés-Belmin, 2011).

The application of the wet poultice was done on the dry surface. Its thickness must be about 2 cm. After the complete drying, the poultice detached from the surface. In the laboratory, the application of poultice was done at 20°C and 50% R.H. for two weeks (Lubelli et al, 2010). In the field, the drying lasted longer than expected. The poultices, which were prepared by Bourgés et al (2008) dried after 5 months depending on the environmental conditions.

The efficiency of the poultice was measured in different ways. Some calculations were done on the amount of salt extracted and the amount originally present in the material. Some measurements were conducted on the type of the ions extracted as well as their amounts to follow the efficiency because the efficiency of the poultices on the type of ions may vary (Bourgés et al, 2008). The poultices done by Bourgés et al (2008) had no efficiency on SO_4^{2-} except kaolin-sand poultice which had low efficiency (Figure 1.7).

1.5.1.3 Vacuum fluid impregnation

The technique based on the “convective transportation” of soluble salts. In this technique, the flow of water was applied through the masonry units by drilling small holes. The water diffused from the back of material towards the surface with the soluble salts. The water moving inside the brick carried the salt solution to the surface by the help of a vacuum system attached (Friese, 1991). That technique was rather destructive to the masonry.

CHAPTER 2

CASE STUDY: DESCRIPTION OF THE HISTORIC BUILDINGS AND THEIR MATERIALS

Seljuks started to settle down in Anatolia after Manzikert War against Byzantine Army in 1071. They stayed on the boundary of Byzantine Empire causing them to put off constructing center of sciences for education until the beginning of 13th century. The center of sciences were called medreses (Kuran, 1969).

According to Kuran (1969), the name of medrese is derived from the action of “lesson” which means that “building used for teaching science” or “university”.

2.1 Brief History of Tiles in Anatolian Seljuk Architecture

In Anatolian Architecture brick started to be used after the second half of the 12th century in Anatolian Seljuk architecture. Simple brick masonry and cut brick for decorative purposes were used and developed. Important differences between the two techniques were the shape of the bricks and the brick patterns. However brick was not the main material for all types of constructions. In addition stone was used and it gained importance after the second half of the 12th century (Ögel, 1966).

The beginning of the production of tiles in Anatolia is after the arrival of the Seljuks. New types of structures were decorated with ceramic tiles instead of mosaics employed in Byzantine architecture. The new style was created by the influence of

Abbasid, Karakhanid, Ghaznavid and Fatimid art in Anatolia in the 13th century which become more important than daily use materials as ceramics. By the considerable effect of the Great Seljuk tradition in İran, the tile decoration reaches a unique aesthetic development under the Seljuks in Anatolia. The concept of using tiles to decorate mosques, mescids, mausoleums, and palaces became characteristic of this period and had a long-lasting effect on the architectural decoration which was extensively used for the interior sides of the monuments (Tapan 1983, Kuban, 2008).

2.2 Use of Tiles on Buildings

Architectural decoration has two main basics. First one is the structural needs and the second one is aesthetic and symbolic needs and values. Using fired brick and glazed bricks were used for the purpose of protection and this was an old technique to make the wall more durable against water penetration. In addition it was widely used for decoration because of their color and arrangement on the wall surface (Kuban, 2008; 338). They were also durable construction materials which were preferred for exterior decoration while tiling remains an interior decoration element (Öney, 1978). Thus it was extensively used for the decoration of minarets. İnce Minareli Medrese in Konya, Çifte minareli Medrese in Erzurum and Sivas Gök Medrese are good examples (Kuban, 2008).

The Seljuk tiles were used on *minarets* as rectangular, square and circular glazed bricks. The smaller cut pieces were used as mosaic and tile mosaic. Mihrabs, walls, eyvans and arches were covered with mosaic tiles, tiles and glazed tiles in mosques and mascids. *Portico* faces, *eyvan* walls and *vaults* were covered with the same kinds of tiles. Mihrab was covered with mosaic tiles which is a contribution of the Anatolian Seljuks to architecture. Domes and transition elements to domes were decorated with mosaic and glazed tiles (Öney, 1976).

Tiles were not as thick as bricks. On the surface they were placed between the vertical jointing and they were not placed deep as bricks because of the thickness. For that reason it was used recessed brick units or special small brick fragments behind tiles which were probably used for the strengthening of brick patterns in case of the breakings (Bakırer, 1981).

Jointing were the horizontal and vertical connecting points between the brick masonry. They did not have special dimensions. They were filled with tile fragments or only with mortars. A limited number of mortar samples from the joints were analyzed in METU Materials Conservation Laboratory. The analysis showed that the mortar was composed of lime and gypsum before and during the Seljuk period in Anatolia. Due to the limited number of samples, the evaluation was also restricted but it was used as lime mortar in brick masonry and gypsum mortar in the ornamented jointing and geometrical arrangements in the brick masonry (Bakırer, 1981).

According to their production and use there were three main types of tiles (Öney, 1978).

- **Plain ceramic tiles** were used for covering the interior walls in Seljuk architecture. Their surfaces were covered with colored glazes. They were approximately 10.5x10.5cm square, star shape or hexagonal with the horizontal placed sides elongated. In addition the sarcophagi from the period are covered by faience mosaic of monochrome plain tiling (Öney, 1978).
- **Faience mosaic** was a Seljuk contribution to the art of Asia Minor. Seljuks developed and used it on the interior decoration element. These were formed by cutting tile pieces to desired shapes for the pattern. The back sides are conical where it is cemented and placed into the wall or the architectural element. The technique was used for the ornaments of mihrabs, inner surfaces of domes, transition to domes, arches, niches and walls (Öney, 1978). Their shapes and sizes vary according to the patterns.

- **Luster, underglaze and minai tiles** were used for the decoration of palaces unlike the religious building decorations in many aspects. Their shape is different as star and cross-combination. Also the type or technique is different as underglaze painted tiling. Lastly the decoration on the tiles is different (Öney, 1978).

Sivas Gök Medrese (1271) and Tokat Gök Medrese (1275) were chosen for the study due to various reasons. The first one is the historic, technological and aesthetic importance of the medreses which are coming to these days from 13th century. The second one is that the buildings had wrong restoration interventions in time. Thus they were nearly losing some of their features such as deterioration and loosening of tiles on the eyvan wall surfaces, powdering of bricks of the medreses. The third one is that the effects of restoration interventions are easily observed in order to get samples from deteriorated materials and salts on the efflorescence zone. Thus, it was understood that the main deterioration factor was efflorescence and the study focused on the salt problem of materials mainly as tiles, their mortars and bricks.

In this part, Sivas Gök Medrese and Tokat Gök Medrese which had different decay problems were described in more detail. It was necessary to summarize their historic backgrounds, materials properties and conservation interventions up to these days. They were useful for the evaluation of the deterioration forms and the proposals of conservation interventions.

2.2.1 Sivas Gök Medrese

Type: This is an open courtyard four eyvans plan type Medrese (Figure 2.1) (Kuran, 1969).

Location: The Gök Medrese is located on the eastern side of Castle and the corner of Medrese Street in Fevzi Çakmak Avenue in Sivas (Tuncer, 2008).

Construction Date and Period: 670 H/1271-72, in the period of III. Gıyaseddin Keyhüsrev who was the son of IV. Kılıç Arslan and the emperor of Seljuk Empire (1265-1282) (Kuran 1968, Bakırer, 1981 Kahya et all, 2002,).

Donor: The command of Vizier Sahip Ata Fahrettin Ali Hüseyin (Kuran 1969, Kahya et all, 2002).

Inscriptions of the Monument: The inscriptions of the portal of monument and mihrab of portal showed the date and construction period. The two sides of the minaret had also inscriptions (Bakırer, 1981).

Architect of the Monument: The name of the architect was signified as "Amel-i Üstad on the southern side and "Kalûyanü'l Konevî" (Konya'lı Usta Kaluyan'ın işi) on the northern side of the inscriptions on the entrance eyvan" (Kahya et all, 2002).

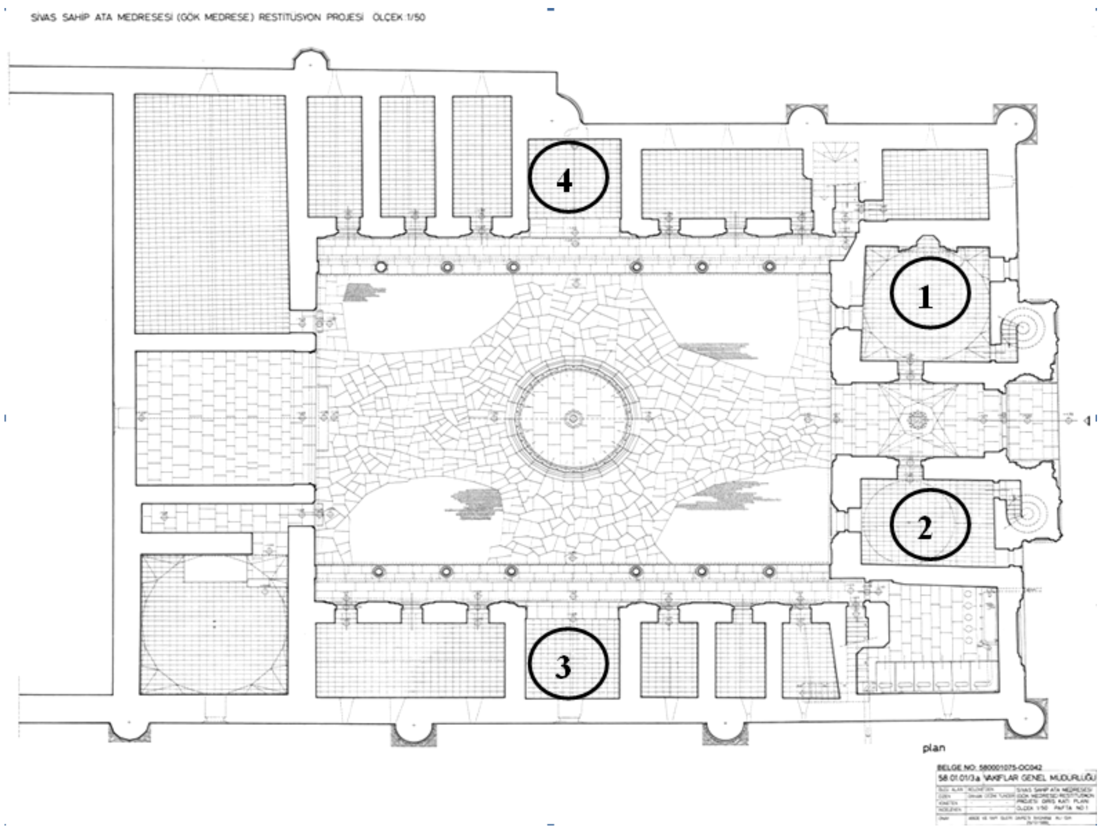


Figure 2.1 Plan of Sivas Gök Medrese. The spaces 1, 2, 3 and 4 have tiles.(Vakıflar Genel Müdürlüğü, 2010).

Architectural Properties of Sivas Gök Medrese

The medrese has a dimension of 1280 m^2. The three sides are surrounded with open areas. It has a rectangular plan having four eyvans and was designed as 'medrese with open courtyard' (Tuncer 2008, Kuran 1969).

Although the courtyard was seemed to be symmetrical, the larger rooms on the east side of south eyvan were not. It was controversial that they were original (Kahya et all, 2002).

The north and south sides of the courtyard have colonated porticoes and eyvans. There were three rooms on one side of each eyvans. The rooms on their other sides were turned into a single space by demolishing the side walls (Kahya et all, 2002).

There was a mescid flanking the south side of the entrance eyvan. The mescid had a mihrab around with tiles and the Turkish triangles on the transition zone which were also constructed with mosaic tiles.

The northwest side of the medrese had toilet (lavatory-abdesthane) having water drainage system. In addition there were some hypotesis that a pool was in the courtyard of the medrese by Önge (1997).

It was accepted that there were pressed earth cover on the vaults as a roof. In addition, according to Tuncer's evidences it is assumed that the exterior tambour of dome and the roof were covered with tiles as regarding the glazed green colored tile findings of the excavations in 2000.

The front façade of medrese had a portal and two minarets. The portal was decorated with geometric and plant figures together with inscriptions. The motifs with glazed tile were lost on the footstall of minarets (Kahya et all, 2002). It was still controversial that the monument had one or two storey (Kahya et all, 2002).

Construction Materials of Sivas Gök Medrese

Sivas Gökmedrese was constructed with rubble stone and the external parts were covered with cut stone. Its interior and exterior sides of the walls were stone but bearing, transitional elements and superstructure are stone and brick. Also its domes were constructed with brick (Bakırer, 1981, Tuncer, 2008, Kuran, 1969).

Brick was not seen in the substructure (Bakırer, 1981). The first floor was limestone and marble. The portal was constructed with white marble together with white veined blue-grey limestone. Also its ground floor was grey veined marble (Kahya et all, 2002).

The courtyard has two colonnaded porticoes on the northern and eastern sides which were also limestone. The upper side of the minarets was covered with brick and glazed brick and eyvans of each side, mirror of vaults, mihrab and tambour of dome were covered with blue and purple tiles. Up today it is conserved only some of the original unique properties such as marble entrance and the order of location in western side (Tuncer, 2008, Kuran, 1969).

The medrese bricks have definite sizes as whole and half bricks. They were used together in the interior sides and the transition elements which stand in a horizontal sequence. The dome and vaults on the superstructure was had also the same arrangement. In addition, the minaret had also bricks on the exterior side, transition zone and the body (Bakırer, 1981).

Today (in 2011), the medrese was under restoration. The walls were covered with new restoration materials and original materials behind the new ones were not clearly seen in the interior side of the medrese.

The Distribution of Tiles at Sivas Gök Medrese

Sivas Gökmedrese had glazed bricks and tiles in different parts of the interior facades and the exterior side. They partly survived until today.

In the medrese, tiles are used in the north and south eyvans and on the mihrab in mascid. These surfaces covered with mosaic tiles and plain tiles. The vaults of the eyvans covered with geometric and plant figured decorative compositions delineated with mosaic tiles. Today, most of them have lost and the empty spaces of the tiles are filled and painted reminiscent to tile revetments in both of the eyvans. In addition, the dome of the mescid on the northwest side of medrese is covered with glazed bricks with tiles inserted in the joints. As these spaces were under restoration, the original tiles and glazed bricks could not be seen clearly.

The materials adjacent to the tile system of the wall are critical factor for conservation. In the monument brick is the main material behind the tiles. Also, the tiles used between the glazed bricks are laid in a bond. Tiles are also placed between unglazed bricks on the minaret, on the dome of mescid and the eyvan vaults. They were fixed onto the white stucco ground at the dome, vault and mihrab (Özçilingir, 1997).

In the outer sides of the medrese, minarets are decorated with unglazed bricks and tiles that are used together (Özçilingir, 1997, Bakırer, 1981). The tiles of the minarets have distinct shapes at their rear sides. They are cone shaped for better attachment with mortar that makes them sounder as regarding to others on the exterior walls. In addition, the tiles are made of weaker materials than that of the bricks. So in time they deteriorate and break faster than the bricks (Bakırer, 1981).

2.2.1.1 Restoration History and Conservation Applications of Sivas Gökmedrese

The documented repair history of Sivas Gökmedrese was important to understand the destructive nature of the changes on historic medieval structures (Kahya et all, 2002). Medrese lost its original form because of demolished main eyvan and inappropriate restoration studies (Hersek, 2001).

The main restoration studies of Medrese:

In 1650, Evliya Çelebi mentioned on "Seyahatname" about the medrese which was destroyed in time in 17th century (Seyahatname, referred by Kahya et all, 2002). The reason of the destruction of eastern and southern facades might be due to the earthquakes in 17. and 18. Centuries (Kahya et all, 2002).

The original appearance of the medrese had changed because of the collapsed parts and some improper restoration applications [Hersek, 2001].

- In 1823-24: Restoration was financed by mufti and professor (müderris) Seyid Abdullah Efendi. Part of the main eyvan was renewed with timber and east and side spaces were excluded from the medrese by a wall which was documented with an inscription (Hersek, 2001). The colonnaded portico in the northwest side and the wall behind were removed and reconstructed (Kahya et all, 2002).
- In 1904: The monument was repaired in an unknown context by Evkaf Vekaleti (General Directorate of Foundations) (Uzunçarşılı et all, 1928 referred by Kahya, 2002). According to the information given by local people, the existing timber gate was put there during Abdülhamit period (Özdural, 1968). Also a pool was constructed in 1904. Then it was used as storage for the military and as a high school. In 1926, the medrese was turned into a museum (Kahya et all, 2002).

- In 1937: The two storeyed house in the main eyvan was pulled down, as a result the foundation walls of the eyvan showed the traces of a mihrab. Also, the mudbrick rooms on the second level of northwest section and the mudbrick partitions in the library and walls facing the courtyard were also pulled down. There was not any tile decoration underneath the plaster of library. The restoration studies could not be completed due to the financial problems (Özdural, 1968).
- 1978-79: Some unsatisfactory repairs were done. The roof was removed for two years because of the suspended payment which causes irreversible damages on material and also the structure. Also, the stones on the front façade of the courtyard were numbered with oil paint. Also in the same years a steel metal roof cover was used which causes color change on the stone façade with rust stain (Kahya et all, 2002).
- 1995-96: Some cleaning research work was done under the leadership of Burhan Bilget (Kahya et all 2002).
- 2008-present: According to the observations, reconstruction of minarets was done. The main eyvan was also under reconstruction. The roof was under construction for renewing. The lost parts of the tiles were infilled and painted for the imitating the tiles (November 2010). The studies were under the control of Turkish Directorate of Foundations.
-

All of these repairs and interventions damaged the tiles resulting in the loss of many of them. The comprehensive repair works have been completed on the north and south eyvans. Indeed, the lost parts of the tiles were filled and painted. However, leaks from the uncompleted roof caused moisturizing of the walls of south eyvan and resulting in the salt crystallization of walls. Also, the moisture causes the flaking off the paints.

2.2.1.2 Tiles Affected from the Structural Problems

The in situ tiles are only partially conserved because of improper and careless restoration applications. Today, the identification of the original tiles in the eyvans is difficult among the painted tiles. Also, the moisture coming from the roof damaged the new material adjacent to the original tiles.

The tiles and glazed bricks on the dome were under restoration. Their originality is not clear because the tiles mostly lost on the mihrab, and the empty spaces are filled with mortar.

2.2.1.3 Conditions before Restoration and Recent Restoration Studies of Sivas Gök Medrese

The last restoration studies of the tiles of Sivas Gökmedrese were done by 'Art Restorasyon Kültür Sanat ve Araştırmacılık Tic. Ltd'. The details of the study were gathered as presentation from Sivas Vakıflar Bölge Müdürlüğü in 2011. The study was based on the protection and restoration of original materials and tiles. In the report, the condition of medrese before the restoration was explained.

Figure 2.2 General view of Sivas Gök Medrese (2011)

The **minaret** consisted of the pedestals which were covered with circular and square shapes with mosaic tile decorations. They were covered with cement-based mortar. The minarets were covered with brick, glazed bricks and mosaic tiles which were partly detached from the body of the minaret. Moreover, the lost parts below the minaret balcony were covered with the cement-based mortar. They were attached to the body of the minaret with iron rods. For this reason, there was detachment and loss of tiles. Glaze of bricks were detached and lost on the body of the minaret. Furthermore, the bricks were deteriorated and the deterioration was more on the north minaret.

Eyvans were covered with mosaic tiles. A wooden skeleton was constructed in the North eyvan to prevent the loss of tiles which were flaking away in 1970s. A hairfelt was put between the skeleton and tiles to prevent the loss of tiles. In time, the tiles were moved away for about 20 cm and sat on the hair-felt of the wooden skeleton. Therefore, it has reached to the present day. In addition, stove and chimney openings on the eastern and western walls have led to the destruction of the parts of the tiles on the wall. Moreover, severe shifts of the monument on the ground had affected the structure. North eyvan had also the same problems, however; the breaking parts were more common in the vault.

In the **mescid,** there was a mihrab which was covered by mosaic tiles. The large parts of the tiles were missing and it was filled with cement-based mortar. Also, the remaining tiles were covered with oil paintings. Furthermore, the loss of the brick and tiles were seen in the dome of the mescid. The mihrab tiles were mostly lost and their places were covered with cement-based mortar.

In restoration project report, cleaning was proposed with two stages:

1. Mechanical cleaning of local filling materials such as cement mortar.
2. Surface cleaning due to the atmospheric reasons were done with the formula of 'AB57'. Then, the surface was colored as the original form of the tiles.

The report mentions about the restoration materials and methods used for each space as minaret, north and south eyvans and mescid. According to the presentation,

- Wood pulps were compressed for salt cleanings where efflorescence was visible.
- Lime mortar was used as mortar. Water-based epoxy was used in some parts
- Polyfilla Exterior* was used for surface covering of original tiles and restorated parts.
- Malta 6001, Malta 6002 or hydraulic mortars were used for the attachment of tile body and plaster to the structure.
- Paraloid B72 was used for surface consolidation in different concentrations (5-30%)
- Primal AC33 was used for the stcking of glazes to body

* "A powder filler which is based on high strength cement and special resins to promote powerful adhesion, toughness and impact resistance for exterior repairs" http://www.icipaints.co.uk/products/info/polycell_trade_polyfilla_exterior_filler.jsp

2.2.1.4 Present Condition of the Monument

Only a portion of the original qualities of the monument could survive to these times. Only the marble entrance portal and the order of the west space were conserved. The rooms of northern and eastern sides seem to be intervened. The main eyvan on the eastern side had collapsed together with the adjacent spaces where it was narrowed down with a wall (Kahya et all, 2002).

The monument was studied during the field trip in November 2010. At that time, the restoration studies were not finished (Figure 2.2). The minarets were repaired, and the interior side of the medrese was still under restoration. In this context, eyvans and the domes were repaired with new materials. The main eyvan was also under construction. In addition, the cut stones of medrese were partly changed with the new ones.

The empty spaces of the lost tiles on the domes were filled and painted reminiscent to tile revetment. The roof system was not finished, so the eyvan walls were moisturized because of rain penetration. Darker color noticed on the eyvan walls was accepted to be evidence for this (Figure 2.3).

Figure 2.3 General view of South Eyvan; Sivas Gök Medrese (2011)

It was informed by local authorities that the madrese is going to be a museum where archaeological findings recovered in an around Sivas will be on display.

2.2.2 Tokat Gök Medrese

Type: This is an open courtyard two eyvans plan type Medrese (Figure 2.4) (Kuran, 1969).

Location: The Gök Medrese is located on Tokat Meydan Street, Gazi Osman Paşa Avenue.

Construction Date and Period: Gabriel dated it back later than 1275 (Kuran referred to Gabriel, 1969).

Donor: It is argued that the medrese was constructed by vizier Muineddin Pervane (Kuran, 1969).

Inscriptions of the Monument: It has no inscription.

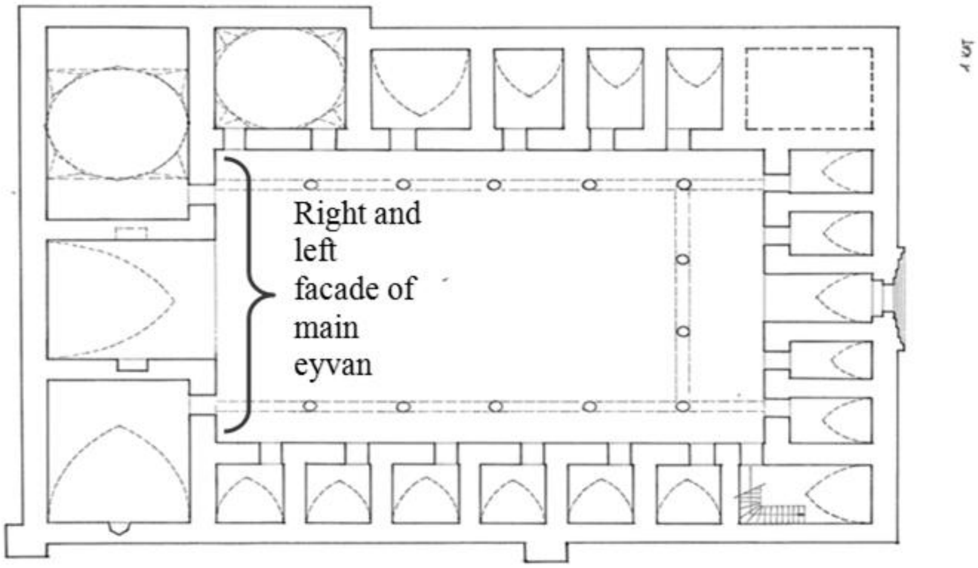


Figure 2.4 Plan of the Tokat Gök Medrese with 1/10 scale (General Directorate of Pious Foundations, 2010)

Mosaic tiles, plain tiles and glazed bricks were used in the medrese. On the façade of the eyvan, two storey high portico façade with arches and on the intrados of the arches, tiles can be noticed in the joints between bricks.

The relation of tiles with the structural material is important. They are used in the common bond brickwork. They are placed in the jointing inside the white stucco mortar ground. It is seen that all techniques and shapes of tiles are used in different parts of the madrese. Bricks are placed besides the tiles, on portal; turquoise colored tiles were implanted into the stone (Özçilingir, 1997).

Kuran has stated that the facades of the courtyard were covered with glazed brick (Kuran, 1969).

The tile decoration is composed of four different orders:

- Simple revetment of turquoise blue hexagonal and eggplant purple triangular tiles
- Turquoise blue tiles used in flower designs and 'sülüs' typed calligraphy

- Turquoise blue and dark purple tile used in strap work
- Mosaic tiles used on the muqarnas half dome of the portal

Architectural Properties of Tokat Gök Medrese

It is the only living medrese having two storeys in Middle Anatolia which reflects the spatial characterictics of similar medreses (Kuran, 1969).

It had two eyvans as entrance eyvan and main eyvan. The two sides of entrance eyvan had rooms having barrel vaults. The south side had six, north side had three and the east side had four rooms (Kuran, 1969).

The saloon on the northern side of the main eyvan was used as a mescid or classroom. The other one was a tomb (Kuran, 1969).

Today the elevation of street was raised so the multi-step staircase leads to the basement of Gökmedrese. The entrance eyvan had the barrel vault with the portal of the medrese. The two sides of the first storey were covered with colonnaded porticoes and the second one was with a gallery (Kuran, 1969).

Construction Materials of Tokat Gök Medrese

The monument was constructed with cut stone. Its interior and exterior sides of the walls were stone but bearing, transitional elements and superstructure were stone and brick used together (Bakırer, 1981). Its portal has two different colored stones which are red and white.

Brick was the main material of the substructure of the monument which preserves its original form. They were horizontally sequenced half bricks. Furthermore the bricks of superstructure and transitional elements were completely restored. The half bricks, glazed bricks with tiles inserted in the joints were used in the horizontal sequence in transitional elements of the monument (Bakırer, 1981).

2.2.2.1 Restoration History of Tokat Gök Medrese

The medrese was found in a bad condition in XIX. Century. It was restored and used as a museum (Kuran, 1969). The original character was mostly lost during the restoration period. On the other hand, portal is still in the original composition which made of light brown colored stone. The carrying walls were mostly constructed with rubble stone (Tuncer, 2008, Kuran, 1969).

The building is used as a museum. It is informed from the official web site of Tokat Governor that the building has been a museum since 1926. Most of the tiles on the main eyvan walls were lost and cement-based plaster was applied on that parts. Some tile fragments nearly lost. Some local repairs were seen.

2.2.2.2 Tiles Affected from the Structural Problems

The tiles are partially conserved and local interventions are seen on the whole surfaces of the interior side of the medrese. The main eyvan façade tiles are exposed to dampness from drainage problems. Thus, they seem to be more damaged with respect to the other tiles of the medrese. They are not very sound and still damaging. The interior sides of the main eyvans seem to be dry and sounder (Figure 2.6)

Today, the medrese is used as a museum for the exhibition of archaeological and ethnographic pieces and coins. The main eyvan walls were covered with cement and limewash (Figure 2.5). The plain tiles of the facades are mainly lost. Although the in situ tiles of the front façade were partially lost, most of them are on the wall. The repairs applied locally on certain spots that were in need of immediate care were not successful.

Figure 2.5 General view of Tokat Gök Medrese (2011)

Figure 2.6 Left wall of main eyvan. Plain ceramic tiles were mostly lost (2011).

2.3 Climatic Conditions of Sivas and Tokat

The climatic conditions of the regions were important parameters for the salts in the materials of the monuments because increasing cyclic dissolution and crystallization-recrystallization of salts causes damage to be more severe. For that reason, it was important to estimate severe effect of the salt crystallization cycles, by the changes in R.H. conditions. The equilibrium relative humidities of some salts at 25°C, 20°C or 18.5°C were given in Table 1.1. The temperatures belonged to spring-summer seasons. For that reason, the discussion of the relative humidity (%) changes was done on one of the summer days of Tokat and Sivas. The climate of Tokat and Sivas were investigated to see the R.H. differences in a day. In general, August was the hottest month for Turkiye. The lowest and highest Relative Humidity values of the regions were examined. The maps in Figure 2.7 show the R.H. variations of 23-24 August 2011 in summer time.

During August 23th, while the R.H. was changing between from 60-70 % to 90-100% in Tokat, Sivas had more sharp changes of R.H. from 40-50 % to 90-100 %. During the R.H. changes, temperatures were ranging between 12.2°C to 28.5°C for Sivas and 15.6 °C to 29.5 °C for Tokat. The temperature variations were taken from the average recordings (dmi.gov.tr).

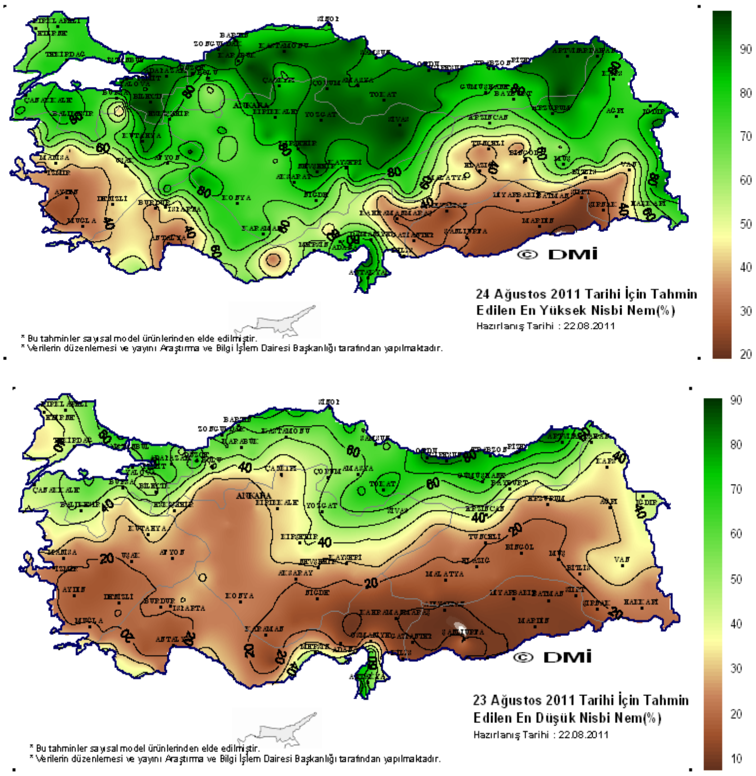


Figure 2.7 The lowest and highest relative humidity values of Turkiye belonging to 24 August 2011 (www.dmi.gov.tr).

CHAPTER 3

EXPERIMENTAL METHODS

In the study, the two selected monuments were studied by starting with the documentation of the present condition of historic tiles.

Mineralogical compositions, petrographical characteristics of the tile body and glaze, adhesive tile mortars of Sivas Gökmedrese and Tokat Gökmedrese were analyzed by X-Ray Powder Diffraction (XRD) and analyses of thin sections by optical microscopy. Their microstructure and chemical compositions were further analyzed by using Scanning Electron Microscope Electron coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDX).

The investigation methods of study were explained in detail under the subheadings as sampling, mapping of visual decay forms, sample collection and their description, basic physical and physicomechanical properties, raw material properties of tile body and mortar, Mineralogical and petrographical analyses, qualitative and quantitative analysis of soluble salts and comparison of salts with the climate of the environment.

3.1 Sampling

Some studies were conducted in Materials Conservation Laboratory in previous years which includes studies on the basic physical properties of tiles, their raw material properties and construction techniques. Also moisture and salt crystallization problem of the tiles were investigated (Özçilingir-Akgün, 1997, Demirci et al, 1996). In this study, the samples from that previous work and newly collected samples were analyzed. In addition, a small piece of original brick sample from the laboratory archive taken in 1973 was also examined. The salt samples and the original brick samples from those monuments were collected in November 2010 with the permission of "Vakıflar Genel Müdürlüğü".

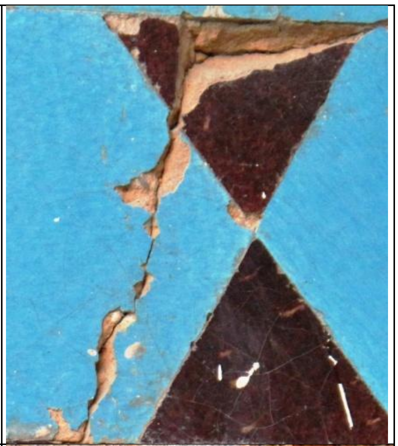
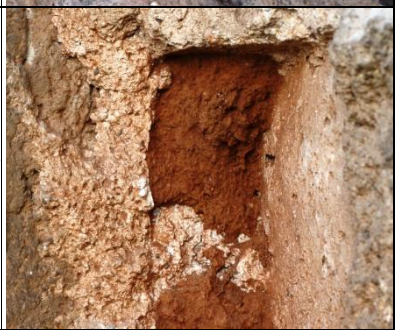
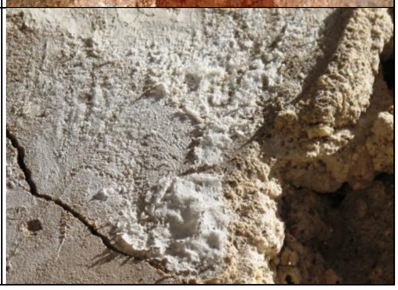
3.2 Mapping of Visual Decay Forms

Mapping of visual decay forms was done during field trip to Tokat Gök Medrese in November 2010. Deteriorations were observed in tiles and brick masonry materials. The deterioration forms of tiles were classified as detachment of tiles from tile mortar, loss of glaze, glaze cracks and tile cracks. The deterioration forms of brick masonry were classified as loss of bricks by crumbling and efflorescences. Each deterioration form was photographed and its location was given.

Table 3.1 The deteriorated tiles and deterioration in brick masonry materials

Materials	**Deterioration Forms**	**Definitions**	**Photographs**
Tiles	Deteriorations of tile, glaze and mortar	Detachment of tiles from adhesive tile mortar	
	The deteriorations were clearly observed in TGM. However it could not be detected in SGM because of the repairs and completion of tiles	Loss of Glazes	

Table 3.1(Continued)

		Tile Cracks	
Structural Materials	Deterioration of brick and mortar behind the tiles **Loss of bricks** could be detected in TGM together with crumbling bricks, but it could not be detected in SGM.	Loss of bricks behind tiles	
	Crumbling bricks together with its loss could be observed in window frame of SGM. They could also be observed in eyvan walls of TGM.	Crumbling and loss of bricks	
	Efflorescence was clearly seen on the walls of SGM.	Efflorescence	

Sivas Gök Medrese

It has been under restoration, but the studies were given up because of the winter (Figure 2.2 and Figure 2.3). Only some site conservation studies around the monument were still going on. In the medrese, the missing parts next to the original in-situ tiles were covered with imitation tiles as new restoration materials. Therefore, it was difficult to observe the deteriorations on the original tiles. The original tiles were surrounded with new restoration materials and imitation tiles are shown in the figures. The new restoration materials were in contact with the original tiles in Figure 3.1. Figure 3.2 showed the painted imitation tiles which were detached. The painted imitation tiles and the original ones were difficult to differentiate by eye. Although they were new, their deterioration has started.

Figure 3.1 North Eyvan wall and dome. New restoration material was in contact with the original tiles and florescence was seen

Figure 3.2 North Eyvan wall and dome. Painted imitation tiles were detached and the original ones were not differentiated by eye.

Tokat Gök Medrese

The interior and entrance façades of main eyvan were covered with faience and mosaic tiles which were mostly deteriorated over time. They were detached from tile mortars. Also glazes of the tiles had cracks and they were partially lost. The mosaic tiles were also lost as blocks. Some of their places were filled with repair mortars, but it was seen that they gave harm to the neighbouring tiles and bricks. As could be seen, the brick which was behind the new mortar was crumbling. The visible parts of the crumbling bricks were also recorded in the table. Also, the walls of the main eyvan and window frames and surface of colonated porticoes were covered with plain ceramic tiles, glazed bricks and tiles on the jointing (Figure 2.6). The interior sides of the main eyvan walls were covered with plain ceramic tiles which were mostly lost.

Mapping of visual decay forms was done with AutoCAD on the façade of main eyvan on its photograph. The photograph was not rectified (Figure 4.1).

The mapping of visual decay forms included six categories. They were ‘loss of tiles from its mortar’, ‘loss of glaze’, ‘loss of tile blocks’, ‘partial loss of tile blocks’, ‘crumbling and loss of bricks’, ‘detachment of tiles and the tile blocks’ and ‘new plaster layer’.

- *Loss of tiles from its mortar:* The decay form was the result of weakening of adhesion between tile body and its mortar. The mortar of plain ceramic tiles was attaching them directly to the wall. The plain ceramic tiles were mostly lost due to that kind of detachment. The mosaic tiles on the wall were seen as tile blocks. The blocks were attached to the wall with a mortar. The mortar of mosaic tiles were keeping them together as tile blocks.
- *Loss of tile blocks:* In-situ mosaic tiles were attached together with tile mortar in a determined composition. Then the tile blocks were attached to brick masonry. In some parts, tile blocks were lost as a whole.
- *Loss of glaze:* Glaze was a protective and decorative layer from external conditions on the tile body. It was detached and lost either with a part of the body alone. It was widely seen in all parts of the tiles in wall.
- *Partial loss of the tile blocks:* Mosaic tiles were sticked together in determined composition with tile mortar. Tile blocks were partially lost in their edges.
- *Detachment of the tiles and tile blocks:* The tile body or tile blocks were detached from its mortar which was noticed clearly.
- *Crumbling and loss of the bricks:* The bricks behind the lost parts of brick mortar were seen that they were crumbled and lost over time.
- *New plaster layer:* The lost parts of the tiles or tile blocks were covered with plaster and lime wash on the upper side of the wall. The plaster layer was in contact with the tiles on the wall.

3.3 Sample Collection and Their Description

In Table 3.2, a nomenclature for the samples was given. In the nomenclature, first letter showed the name of medrese: Sivas Gök Medrese (S) and Tokat Gökmedrese

(T). Second letter showed the type of sample as tile body (B), tile mortar (TM), mortar (M), brick (Br), repair mortar (RM) and salt (S). For example, SB2 was the second tile body sample of Sivas Gök Medrese.

Table 3.2 Sample codes of the medreses and their descriptions

1st Part	Place of Samples	Sivas Gökmedrese	S
		Tokat Gökmedrese	T
2nd Part	Type of Samples	Tile Body	B
		Tile Mortar	TM
		Mortar *	M
		Brick **	Br
		Salt	S
		Repair Mortar	RM
3rd Part	Sample Number		

* Mortar samples were taken from Tokat Gök Medrese in November 2010. It was not known whether they were original or repaired mortars.

** There were two brick samples which were taken in different years. SBr1 was taken in 1973, SBr2 was taken in 2010.

3.3.1 Sivas Gök Medrese

In the field study, the spaces having tiles and glazed bricks were numerated in the plan of Sivas Gök Medrese (Figure 2.1) which was obtained from General Directorate of Pious Foundations in 2010. The walls were numbered in clockwise direction.

1st Space was mescit. Its dome was covered with glazed bricks and the surface of the mihrab was covered with mosaic tiles. The glazed bricks were the painted imitation tiles. The mosaic tiles of the mihrab were mostly lost. 2. Space was Dar-ül Kura. Its dome was covered with imitation glazed bricks. 3. and 4. Spaces were the side eyvans as North and South Sides. They were nearly in the same condition having imitation mosaic tiles together with the original ones. Efflorescence was observed in each wall of eyvans. Also, painted imitation tiles were detached. Samples were collected from 3. and 4. Spaces as North and South Eyvans (Figure 2.1).

Table 3.3 described the samples of Sivas Gök Medrese which were taken in 1973, 1997 and 2010. Tile and their mortar samples were collected from the ground of the courtyards in 1997. Therefore, it can be concluded that the samples were detached and fell down for some reason. Their duration on the ground was not known. The tile samples of Sivas Gök Medrese were still attacted to their mortars (SB1, STM1; SB2, STM2) (Table 3.3). A small brick sample was from 1973 which gave an idea about the original composition of the brick in Sivas Gök Medrese (SBr1).

Table 3.3 Deteriorated tile samples with their mortars collected from the soil ground in 1973 and 1997 in Sivas Gök Medrese

Sample Type	Sample Code	Description	Photographs
Tile	**SB1** **STM1**	The tile fragment and its mortar from South Eyvan. Eggplant purple and turquoise colored glazes on its surface were partly lost. The remaining glazes had cracks. The thickness of the tile body was between 1-1.5 cm and the thickness of the mortar was between 1.7-2.1 cm.	

Table 3.3 (Continued)

Tile	**SB2** **STM2**	Eggplant purple and turquoise colored glazed tile and mortar. There were cracks on the glaze. The thickness of the tile body was between 1.5-0.57 cm and the mortar was with a thickness of 1.3-0.5cm. Its place on the monument is not known. Backside of the tile was cone-shaped and embedded into the mortar.	
Brick	**SBr1**	Two small brick samples which were taken in pedestal of minaret in 1973.	
Glazed Brick	**SGM**	Piece of glazed brick sample from laboratory archive	

In 2010, the restoration studies were almost finished in Sivas Gök Medrese. Salt samples from the eyvan walls, powdered brick sample from the eyvan window and new restoration mortars between the original tiles were collected in Sivas Gök Medrese (Salt; SS1, SS2, SS3, SS4, SS5, SS6, SS7 and SS8, Brick; SBr2, Repair Mortars; SRM1 and SRM2) (Table 3.4).

Table 3.4 The description of salt, brick and mortar samples which were taken in Sivas Gök Medrese in November 2010.

Sample Type	Sample Codes	Descriptions	Photographs
Salt	**SS1**	South Eyvan, 1st Wall, Height: 205-220cm	Their positions were signed on Figure 3.3.
	SS2	South Eyvan, 1st Wall, Height: 190-210cm	
	SS3	South Eyvan, 1st Wall, Height: 180-200cm	
	SS4	South Eyvan, 1st Wall, Height: 145-155cm	

Table 3.4 (Continued)

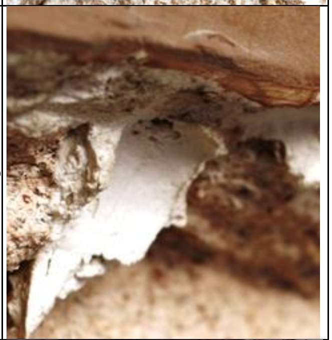
Salt	**SS5**	South Eyvan, 1st Wall, Height: 125-140cm	
	SS6	South Eyvan, 1st Wall, Height: 110-125cm	
	SS7	South Eyvan, 1st Wall, Height: 200-215cm	
	SS8	South Eyvan, 1st Wall, Height: 150-200 cm	
Brick	**SBr2**	South Eyvan, 1st Wall, Interior side of window frame. It was in powdered form.	
Mortar	**SRM1**	North Eyvan, 1st Wall, Interior side of window frame. It was the background of painted imitation tiles.	
	SRM2	North Eyvan, 1st Wall, Interior side of window frame. It was behind the SRM1.	

Figure 3.3 represents the locations of the salt and brick samples on the 1st wall of the South Eyvan. The salt samples were located on the lower part of the wall in which original and imitation tiles were not present but it seemed that the source of water was mostly on the upper side of the wall which was also affecting the original tiles together with the imitation ones.

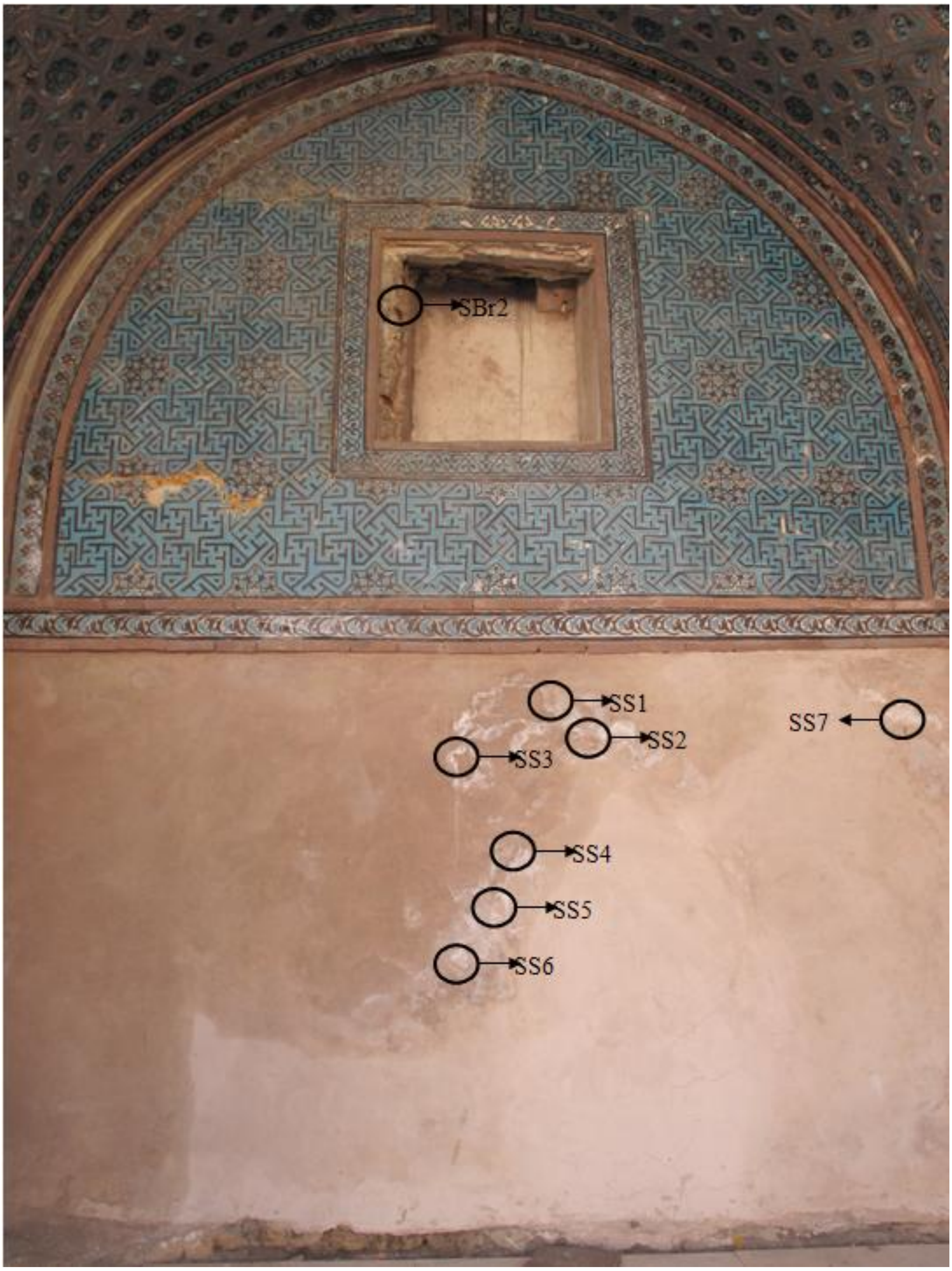


Figure 3.3 The location of salt samples on efflorescence zone and brick samples which were taken in 1st wall of South Eyvan in Sivas Gökmedrese.

3.3.2 Tokat Gök Medrese

In the field, the façade of the main eyvan was studied as shown in Figure 2.4. The façade of main eyvan was shown on the plan of Tokat Gök Medrese.

The plan was obtained from General Directorate of Pious Foundations in 2010.

In Table 3.5, the tile, glaze and mortar samples which were collected from the courtyard of Tokat Gök Medrese in 1997, were described. The tiles of Tokat Gök Medrese were mostly without their mortars (TB1, TB2, TB3, TB4, and TB5) except TB6 with its mortar TTM1.

Table 3.5 The description of some tile samples which were found in the courtyard of Tokat Gökmedrese in 1997.

Sample Codes	Description	Photographs
TB1	Turquoise colored tile body fragments.	
TB2	Turquoise colored tile body fragments.	
TB3	Eggplant purple colored tile body fragments having the thickness were between 1,9-2,3 cm	

Table 3.5 (Continued)

TB4	Turquoise colored tile body fragments having the thickness between 1,48-1,56 cm. The glazes had cracks.	
TB5	Eggplant purple colored tile body fragment having the thickness were between 2,3-2,4 cm. There were glaze cracks on the surface.	
TB6 **TTM1**	Black colored tile fragment and its mortar. The thickness of tile body was between 1.5-1.6 cm. Also the thickness of mortar was between 1.6-1.8 cm. There were glaze cracks on the surface.	

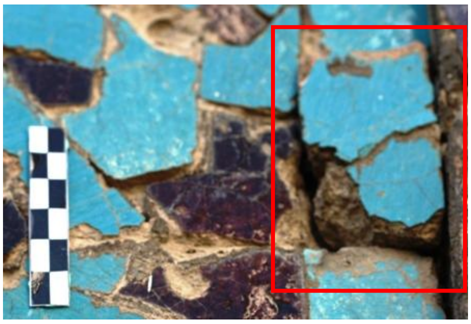
In Table 3.6, the samples which were collected from the main eyvan walls of Tokat Gök Medrese in 2010 were described.

Tokat Gök Medrese had visible local interventions on the wall of main eyvan. Small mortar samples were taken from there which their originality was not known (TM1, TM2, TM3, TM4 and TM5). Also small brick sample, a powdered brick and a detached tile samples were taken on the façade to see the effects of the interventions and also to analyze their deteriorations (TBr1, TBr2, and TB7).

Table 3.6 The description of some mortar, brick and tile samples which were collected from main eyvan walls of Tokat Gök Medrese-November 2010.

Sample Codes	Description	Photographs
TM1	Mortar sample from the left side of the façade of the main eyvan. It was taken at the height of 130 cm. There were powdered bricks behind the mortar.	
TM2	Mortar sample from the left side of the façade of the main eyvan. It was taken at the height of ~120-125 cm. There were powdered bricks behind the mortar.	
TM3	Mortar sample from the left side of the façade of the main eyvan. It was taken at the height of ~100 cm. There were powdered bricks behind the mortar.	
TM4	Mortar with a thin layer of plaster sample from the right side of the façade of the main eyvan. It was taken at the height of ~100 cm. It was applied to the bed of lost tile block.	

Table 3.6 (Continued)

TM5	Mortar sample from the right side of the façade of the main eyvan. They were broken off to the ground.	
TBr1	Brick sample from the left side of the façade of the main eyvan. It was taken at the height of ~105 cm. It was on TM3.	
TBr2	Powdered brick sample from the left side of the façade of the main eyvan. It was taken at the height of ~95 cm. It was behind TM3.	
TB7	Detached tile sample from the left side of façade. It was taken at the height of ~200 cm.	

The samples from the different periods were reflecting the intervention and restoration effects as well as the environmental effects on the two medreses. The results of the analyses were evaluated together.

3.4 Basic Physical and Physicomechanical Properties

3.4.1 Color Measurements

Determination of color was used to distinguish ancient potteries. In the experiment, the colors of the tile body, glaze and mortars were documented numerically. The color measurement was performed by portable Konica Minolta Spectrophotometer CM-2600d/2500d. D65 was used as average solar light. The color differences of glazes, tile bodies and their mortars were detected. Each value was the average nine values of the three different points on the same sample. It should be regarded that the glazes had cracks on them. The colors were indicated in Table 4.1.

In the CIELAB system, color was described as three coordinates: 'L' represents lightness which range from 0 to 100. CIE 'a' represents greenness (negative) and redness (positive) which range from -90 to 70. CIE 'b' represents blueness (negative) and yellowness (positive) which range from −80 to 100 (Commission Internationale de l'Eclairage, 2004). The schematic representation of L*a*b Color Space colors were seen in Figure 3.4.

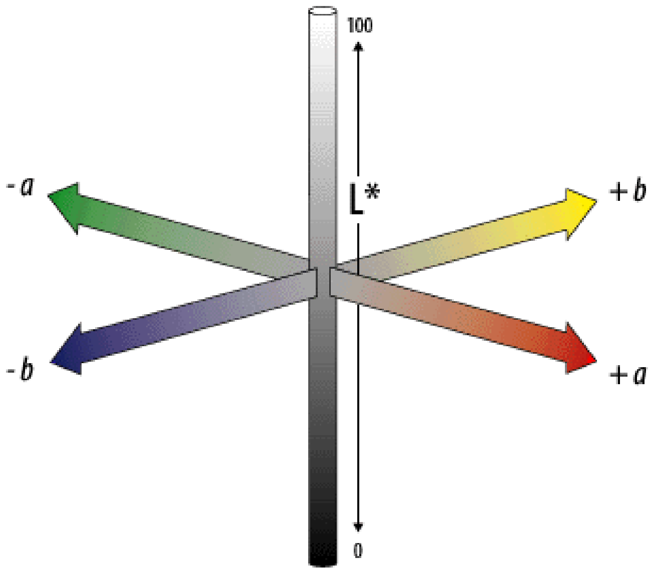


Figure 3.4 Representation of L*a*b Color Space (dba.med.sc.edu)

Specular reflected light of the sample was excluded in the SCE geometry and conversely it was included in the SCI geometries (Lee et al, 2010). SCI values were used for the determination of L*a*b colors of the samples.

3.4.2 Bulk Density and Effective Porosity

Porosity was expressed as the percentage of the volume in the mass. It was calculated by using the formula (3.1).

Density (d) was expressed as the ratio of the mass to the bulk volume of the sample. Its unit was g/cm^3. It was calculated by measuring dry weight, water saturated weight and Archimedes weight by using the formula (3.2).

$$P\ (\%\ volume) = [(m_{sat} - m_{dry}) / (m_{sat} - m_{arch})]*100 \qquad (3.1)$$

$$D\ (g/cm^3) = (m_{dry}) / (m_{sat} - m_{arch}) \qquad (3.2)$$

The measurements were used for the calculation of density and porosity values according to the RILEM 1980 Standards.

The abbreviations were as follows:

m_{sat}: Water-saturated weight (g)

m_{dry}: Dry weight (g)

m_{arch}: Water-saturated weight of sample in water-Archimedes weight (g)

The weights of the dry samples were recorded and then they were saturated in water-filled beakers and waited over a night. The water-saturated samples were weighted and their Archimedes weights were also recorded in water. The measurement was done with the sensitivity of 0, 0001 g. The results were given as mean values with standard deviations (RILEM 1980).

3.4.3 Modulus of Elasticity (Young's Modulus)

The modulus of elasticity was expressed as the ratio of stress to strain (Timoshenko, 1970).

In the study, the modulus of the elasticity of the tile body and tile mortars was measured with ultrasonic pulse velocities passing through the samples. The experiment was carried out by using PunditPlus and E_{mod} values of samples were calculated by using ultrasonic pulse velocities and the densities of samples. The formulas **(3.3)** and **(3.4)** were given as follows:

$$V=I/t \qquad (3.3)$$

V: Velocity (m/s)

I: The distance traversed by the wave (mm)

t: Time of travel (s)

$$E_{mod}=D*V^2(1+ v_{dyn})(1-2 v_{dyn})/(1- v_{dyn}) \qquad (3.4)$$

E_{mod}: Modulus of Elasticity (GN/m^2)

D : Density of the specimen (kg/m^3)

V : Wave velocity (m/sec)

v_{dyn}: Poison's ratio

The tests were done with tile mortars and tile body samples. The dimension of the samples was between 31 and 64 mm. In the case of historic building materials, it was not possible to get sample sizes as required by the standards (RILEM 1980).

Experiment was done with the tile body and tile mortar samples of two medreses. Three points were determined on the samples and their thickness was measured. Five ultrasonic measurements were taken on each point. Their modulus of elasticity (E_{mod}) values was calculated and they were compared with Seljuk Period mortars (Tunçoku, 2001).

3.5 Raw Material Properties of Tile Body and Mortar

In the study, acid and water soluble/insoluble ratios of mortars, particle size distributions of the aggregates and pore size distribution of tiles and their mortars, pozzolanic activity measurements were done and oil, hydrolysable resins and proteins were tried to be detected.

3.5.1 Acid Soluble/Insoluble and Water Soluble/Insoluble Ratios of Tile Mortars

This experiment aimed to see the quantitative estimation of the main components of tile mortar as binder and aggregates on both of the medreses and to get the acid soluble aggregates for size analyzes. The percentage of the binder and aggregates of tile mortars were estimated by using solubility properties of the binder in acidic solution and in distilled water.

The two pieces of each tile mortar samples (4-5 g) were dried and weighted with the sensitivity of 0.0001g. Then, the mortar pieces were dissolved in ~ 200-250 ml 5% hydrochloric acid till the bubbling stoped. The insoluble residue was the insoluble aggregates part of the mortar. It was separated from the soluble part which was the binder of the mortar. The insoluble residue was washed with distilled water and dried in an drying-oven at 40°C and weighted. The percentages of acid soluble and insoluble parts were calculated by using the formula (3.5) and (3.6) (Jedrzjevska, 1981):

$$\% \text{ Insoluble part} = [(m_{samp} - m_{insol}) / (m_{samp})]*100 \qquad (3.5)$$

$$\% \text{ Soluble part} = 100 - \% \text{ insoluble part} \qquad (3.6)$$

where, m_{samp} : Dry weight of the sample (g)

m_{insol} : Dry weight of insoluble part (g)

The acid-insoluble residue was analyzed with XRD which showed that the remaining part was gypsum based mortar. In order to eliminate all the gypsum from the mortar, which may have been used as binder and/or aggregate, 80 ml of boiling diluted HCl was used for about 5 grams of sample. After that, 200 ml of boiling water was added to the boiling solution in order to eliminate the precipitation of sulfates during cooling (Middendorf et al, 1998). The residue was acid-insoluble aggregate. It was dried, weighted and documented with photographs.

The reaction of mortar in HCl was a clue for the presence of calcite. In order to detect the presence of calcite, the slight solubility of gypsum and the insolubility of calcite in water were used. 2.4g of each TTM and STM were ground and dissolved in 1 liter of distilled water in the volumetric flasks with magnetic stirrer. After dissolution, it was filtered and water-insoluble residue was dried, weighted and analyzed with XRD.

The differences of acid-soluble and water-soluble parts were detected and weight differences were calculated as the ratio of calcite.

3.5.2 Particle Size Distributions of the Tile Mortar Aggregates

Particle sizes of insoluble aggregates in tile mortars were determined by standard sieve analysis using 2000, 1000, 500, 250, 125 and 75 μm sieves. The results were expressed as the percentage of each particle size and they were indicated in the diagram (Figure 4.7) as the percentage of each particle size. They were also documented by stereomicroscope photographs for their colors and shapes.

The classification of particles was done according to Tucker (2001). Mineralogical compositions of the particles were done by XRD.

3.5.3 Pore Size Distribution Measurement of Tile Bodies and Their Mortars

Pore size distribution measurement was performed by Mercury Porosimeter. It was useful for the generation of pore size/volume distributions. The physical principle of mercury porosimeter depends on the penetration of mercury to the fine pores under adequate pressure. The applied pressure and pore diameter was explained with Washburn Equation:

$$D=(-4\gamma \cos\Theta)/P$$

Where P is applied pressure, D is pore diameter, γ is surface tension of mercury (480 dyne/cm), and Θ is the contact angle between mercury and pore wall (usually 140°).

The measurement was done in METU Central Laboratory with the instrument Quantachrome Corporation, Poremaster 60. Pressure was applied between ~1 to 30000 PSIA to measure the dimension of pores between ~247 μm to 0,007 μm.

The results were evaluated and compared with the pore size distribution of the poultices in the literature for salt extraction.

3.5.4 Pozzolanic Activity Measurements by Electrical Conductivity

Pozzolanic activity was defined as the the ability to react with lime and or to form insoluble products with binding materials (Baronio et al, 1997). The experiment was used to evaluate the pozzolanic activity of tile body and brick samples of the medreses. It was measured by using electrical conductivity.

Tile body and brick samples (~0.05 g) were ground and the weight was recorded with the sensitivity of 0, 0001 g. They were mixed with saturated calcium hydroxide [$Ca(OH)_2$] solution (30ml) in a plastic containers. The mixed solution was left in laboratory conditions for 14 days. The second step of the experiment was the titration of the solution with EDTA solution. 10 ml of the sample above the container was diluted to 100 ml. The pH of the solution was ~10 by the addition of 2-3 ml NaOH (10%) solution. Also, 3-4 drops of calcon indicator was added to the solution it was titrated with EDTA (0.01M) until the solution turned blue from pink. The consumed volume of EDTA was recorded for each solution. The last step was to calculate the amount of Ca^{2+} by using the volume of EDTA used. The results were evaluated by calculating the solutions' electrical conductivity to use the classification method of Luxan (1989) which was given in Table 3.7.

Table 3.7 Evaluation of pozzolanic activity by conductivity measurement (Luxan, 1989)

Classification of Material	**Variation in Conductivity according to Luxan's method (mS /cm)**
Non Pozzolanic	Less than 0, 4
Variable Pozzolanicity	Between 0, 4 and 1, 2
Good Pozzolanicity	Greater than 1, 2

According to the classification of Luxan et al (1989), the pozzolans having the values of ΔEC higher than 1.2 mS/cm were accepted as good pozzolanic materials. If the values were between 0.4-1.2 mS/cm, it was classified as variable pozzolanicity. The values lower than 0.4 mS/cm was considered to be non-pozzolanic materials.

3.5.5 Detection of Oil, Hydrolysable Resins and Proteins in Tile Mortars

Oil and proteins might be added to the mortar to reduce its solubility. Their detection was difficult because of the lower amounts.

Detection of Oil and Hydrolysable Resins

A few mgs of powdered mortar samples were put in the glass tubes. A few drops of conc. NH_3 to react with hydrolysable materials, giving NH^{4+} salts (fatty acids and soaps etc). A few mgs of H_2O_2 were added to produce gas bubbles and 0, 1 % cupric sulphate solution ($CuSO_4$) was added to act as a catalyst. During 1-2 minutes, gas bubbles were observed (Feigl, 1958). The experiment was done with STM and TTM.

Detection of the Proteins and –CO-NH groups

The test was used for the detection of egg albumin, hemoglobin, casein, salmine, clupeine, serum albumin, edestin and gliadin (Feigl, 1966). As mentioned before, it was difficult to detect the proteins because of the dissociation of proteins by bacteria (Middendorf et al, 2005).

A few mgs of powdered mortar sample and a filter paper piece having 1-2 cm length were put in a glass tube. The filter paper was wetted by a few drops of %5 paradimethyl aminobenzaldehyde in concentrated HCl. The test tube was gently heated by a bunsen burner. Pink-violet color was observed in case of the reaction of paradimethyl aminobenzaldehyde with –CO-NH groups.

3.6 Mineralogical and Petrographic Analyses

Mineralogical and petrographical analyses included the examination of the thin sections and cross sections by optical and stereomicroscopes. In addition XRD analyses, scanning electron microscopy (SEM) analyses coupled with an energy dispersive X-ray analysis unit (EDX) analyses were used.

3.6.1 Cross Section Analyses with Stereomicroscope

Pieces of tiles with their glaze, body and mortars were hardened with polyester resin in the plastic containers (~1,5x3x1cm). After solidifying, the samples were taken in the containers and cut with thin diamond blade ((Buehler-Isomet Low Speed Saw). The cut surfaces were coated with Geofix resin. After drying, the coated surfaces were polished with re-sanding papers (Silicone Carbide 320 and 600). The photographs of the samples were taken with a computer program Leica Application Suite (LAS) with stereomicroscope. Photographs were analyzed for the body, the thickness of glaze, and its interaction with the body.

3.6.2 Thin Section Analyses with Optical Microscope

It was necessary to get the information about the petrographical and mineralogical properties of tiles and their mortars. The samples were hardened with special polyesters with accelerators and hardeners in small plastic boxes (1.5×3×1cm). After complete drying, the removed samples were cut into 1mm slices and attached on glass slides. Their thickness was reduced up to 30 micron.

Thin sections were prepared by M.T.A. (Mineral Research and Exploration Institute). The thin sections were examined qualitatively with optical microscope (Leica DM4500-P) for the mineralogical and morphological properties of tile body, binders and aggregates of mortars.

Binders and aggregates of mortars and temper and matrix of tiles were analyzed for their types, shapes and distribution.

3.6.3 XRD Analyses

XRD analyses were aimed to determine mineralogical composition of tile body, glaze and mortars.

Investigation of the binder and aggregate parts of the tile mortars were adapted from RILEM TC 167-COM (2005). Binder and aggregates were grinded for the qualitative detection of the minerals in binder and aggregates finer than75µ with XRD. The powdered samples were analyzed with Bruker D8 Advance with CuKα radiation. The results were evaluated with DiffracPlus Eva.

3.6.4 Scanning Electron Microscopy (SEM) Coupled with Energy Dispersive Analyzer (EDX)

Characteristics of mortars and their morphologies, microstructures and chemical compositions were investigated by using TESCAN model scanning electron microscope (SEM) to get complementary information about the morphology and microstructure of tile mortars, binder and aggregates and their pores. It was also used to detect salt minerals in the pores.

3.7 Qualitative and Quantitative Analysis of Soluble Salts

In this study, the experiments were performed on the crumbling and partly deteriorated brick, tile and mortar samples. Also, salts on the eyvan walls of Sivas Gök Medrese were taken for the analyses. The types of salts in the sample were determined by spot chemical analysis, cross-sections, XRD and SEM-EDX. Their amounts in the samples were determined with conductivity measurements.

3.7.1 Quantitative Analysis of Soluble Salts

Conductivity Measurements of the Materials

The soluble salt content was determined by electrical conductivity measurements

In the experiment, approximately 1gr of crushed brick and tile samples were mixed with 50 ml distilled water let to settle and tested for the resistivity of the solution (3.7)

(A*50/1000)*(1/Weight of sample(mg))*100=% salt in the sample (3.8)

Where;

R_{std}: Cell resistance with standard solution

R_{ext}: Cell resistance with extract solution

A :Salt concentration mg/liter =640*EC ($mmho.cm^{-1}$)

The highest salt concentrations were taken into account for the experiment.

The extract solutions were used for the qualitative analysis of soluble salts in the water. The water was evaporated and the residue was analyzed.

The conductivity calculations were done by regarding the mineral components of the samples. More specifically, raw materials of mortars were gypsum which was slightly soluble as (0.2g/1000 ml). The amount of salts was calculated by subtracting the soluble gypsum content in a known amount of water. Indeed, the solubility of pure gypsum was calculated without the effect of additives of mortar on the solubility of gypsum (Black, 1960).

3.7.2 Qualitative Analysis of Soluble Salts

The qualitative analyses of samples were done by using different techniques as spot tests, XRD, examination of cross sections by stereomicroscope and SEM-EDX.

Spot tests: For the qualitative analysis of soluble salts in the samples, their anions were detected with simple spot tests (Feigl, 1966) by using the solutions of samples which were used to detect the amount of salts by conductivity measurements. The spot tests included the detection of phosphate (PO_4^{-2}), sulphate (SO_4^-), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-) and carbonate (CO_3^{2-}).

XRD Analyses of Salts: XRD analyses were aimed to determine mineralogical composition of salts. The salts which were taken directly in the efflorescence zone and samples containing high amount of salts were analyzed with XRD. Some salts were extracted from the samples and dried in laboratory conditions or in drying-oven. In order to analyze salt in the sample, the XRD analysis was done before and after washing it to see the difference. Analyses were done with Bruker D8 Advance with CuKα radiation. The results were evaluated with DiffracPlus Eva.

Analyses of Salts of Cross-Sections by Stereomicroscope and SEM-EDX: In order to detect the salt crystals in the pores or on the surface, the cross section of the mortars and small brick samples were examined with stereomicroscope. The detected salt crystals were documented with photographs and analyzed with SEM-EDX to prove their existences.

3.8 Comparison of Salts with the Climate of the Environment

The relative humidity fluctuations caused crystallization-recrystallization cycles of the salts which increased adverse effects of them on porous materials. Salt crystallization cycles depended on the equilibrium relative humidity of the specific salts. The equilibrium Relative Humidity values of the salts were known from the literature at specific temperatures. It must be considered that the salts were generally in a mixed form with the others. Thus, the equilibrium relative humidities of the salt mixtures were lower than their pure forms. In this study, the comparisons were done by disregarding the lowering of R.H in a mixture and the temperature fluctuations in a day. Only the highest and lowest R.H. values were taken into consideration. The temperature fluctuations in a day were omitted.

CHAPTER 4

EXPERIMENTAL RESULTS

Experimental results of this study are given under the titles of "Mapping of Visual Decay Forms", "Basic Physical Properties", "Modulus of Elasticity of the Bodies and Mortars (Young's Modulus)", "Raw Materials Properties", "Petrographic Analyses", "Qualitative and Quantitative Analyses of Soluble Salts" and "Comparison of Salts with the Climate of the Environment".

4.1 Mapping of Visual Decay Forms

Mapping of visual decay forms of Tokat Gök Medrese was done on its digital photograph showing the façade of the main eyvan taken in November 2010. That non-rectified photograph presented the latest as-is situation of the medrese, therefore, it was representative for the recent repairs, typical decay forms and their distribution on wall surfaces. The decay forms were mapped by using the software AutoCAD and the surface areas were calculated for each decay form. The quantitative data on the surface area of decay forms were used to assess the state of deterioration of the surfaces with tiles and their possible sources.

The term "visually-sound" was used in the text to refer to the glazed tile surfaces without material loss, crumbling and detachment. The term "visually-deteriorated" was used in the text referring to the newly-plastered surfaces and surfaces with tiles having visual decay forms.

The calculations were done by using the relative areas of each deterioration type and the total area of the facade. Areas on the façade were evaluated as visibly deteriorated or visibly healthy. The percentages show that the total relatively healthy area was 44.9 % which was less than a half (Figure 4.1).

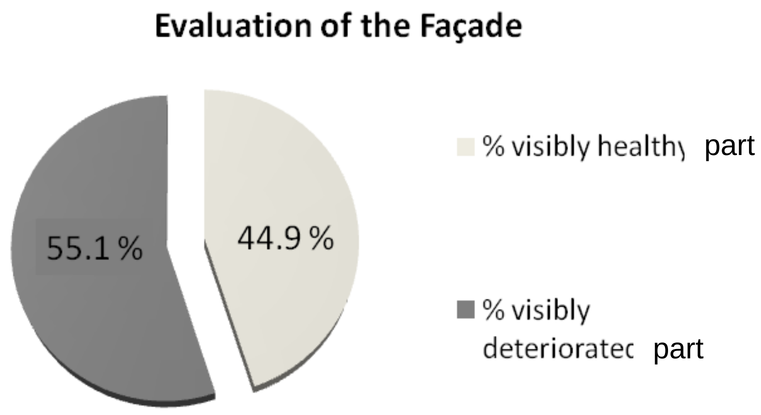


Figure 4.1 Evaluation of the deterioration on façade of Tokat Gök Medrese

The remaining 55.1% area was visibly deteriorated. The visibly deteriorated area had loss of materials as glaze, tile blocks, tiles and bricks. They were calculated as loss of glazes (4.7%), loss of tile blocks (5.3%), partial loss of tile blocks (2.3 %), crumbling and loss of bricks (0.2%) and detachment of tiles and tile blocks (1.5%) as seen in Figure 4.2.

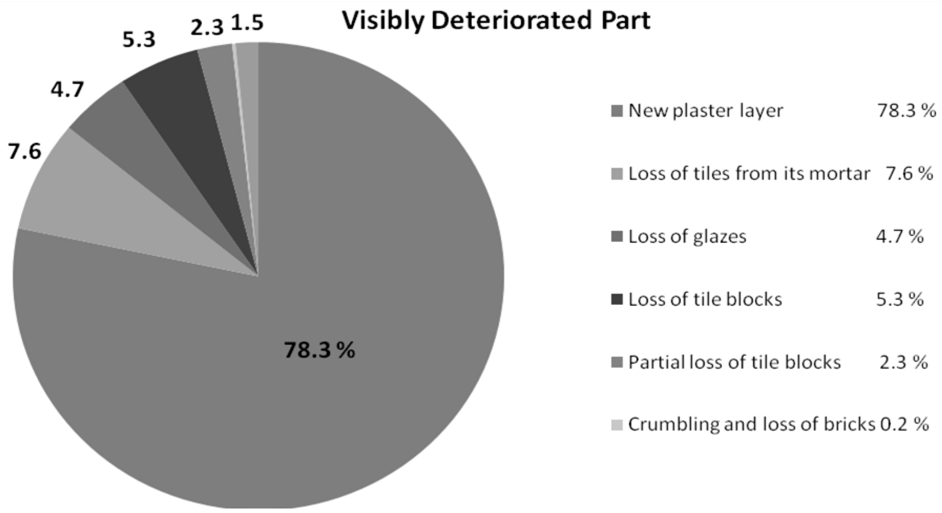


Figure 4.2 The percentage of visual decay forms observed on the façade of Tokat Gök Medrese (with the portion of visibly-deteriorated surfaces 55.1%)

Figure 4.3 Mapping of visual decay forms in Tokat Gökmedrese

4.1.1 Color Measurements

Some L*a*b values of tile glazes, bricks and tile mortar were given in the Table 4.1. Each value was the average of nine values of the three different points on the same sample. It should be regarded that the glazes had cracks on them.

Table 4.1 Calculated L* a* b* values of glazes, bodies and mortars of tiles belonging to Sivas Gök Medrese and Tokat Gök Medrese

	Sivas Gök Medrese Samples (SCI)			**Tokat Gök Medrese Samples (SCI)**		
	L	**a**	**b**	**L**	**a**	**b**
Tile Mortars	86.39	1.39	5.92	80.46	2.07	8.14
Tile Bodies	53.80	8.26	15.07	60.49	11.23	22.82
Black Glazes	24.83	0.64	0.39	23.77	4.69	-2.89
Blue Glazes	48.42	-20.19	-9.17	52.97	-19.88	-9.09
Eggplant Purple Glaze				27.88	1.56	-10.00

According to the table, tile mortars were white-grey colored, tile bodies were light pink and glazes were black, blue and eggplant purple. They were expressed with their L* a* b* values.

4.1.2 Bulk Density and Effective Porosity

In the experiments, at least two tile body and mortar samples for each medrese were used. The samples were rather small. The values were compared with other Seljuk monuments' data.

Sivas Gök Medrese

The bulk density and effective porosity values of tile mortar, body and repair mortars of Sivas Gök Medrese were given in Table 4.2. Original materials were tile bodies and tile mortars. Repair materials were mortars.

The average density of original tile mortars (STM) were 1, 26 ± 0.04 g/cm^3 and their average porosity was 46 ± 2%. The average density of tile bodies (SB) were 1.56 ± 0.01 g/cm^3 and their average porosity was 39 ± 1 %. The repair mortars of Sivas Gök Medrese had the average value of 1.71±0.3 g/cm^3. Their average porosity was 29±0.9 %.

Table 4.2 Bulk density and porosity values of tile mortar, tile body and repair mortars of Sivas Gök Medrese.

Sivas Gök Medrese				
	Original Materials		Repair Materials	
	STM Tile Mortar	**SB** Tile Body	**SRM1*** Mortar	**SRM2** Mortar
d (g/cm^3)	1,26 ± 0,04	1,56 ± 0,01	1,42	1.86 ± 0,03
P (%)	46 ± 2	39 ± 1	30	28 ± 0,1

*Only one piece was available

Average bulk density and porosity values are given in Figure 4.4 in order to compare the tile bodies, mortars and the repair mortars with bricks and brick mortars of twelve Seljuk monuments in Konya.

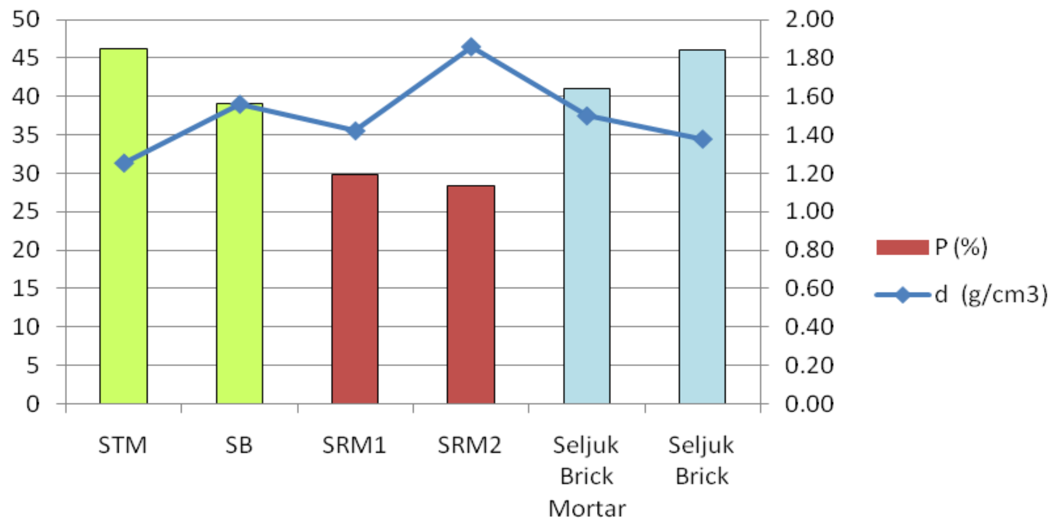


Figure 4.4 Bulk density and porosity values of Sivas Gök Medrese tile mortars, repair mortars and their comparison with other Seljuk Monuments (Green; Tile Mortar and Body samples, Red; Repair Mortar samples, Blue; Seljuk Period brick mortar and brick samples from Tunçoku, 2001).

According to the results, original tile bodies and tile mortars had quite lower bulk density and higher porosity than the repair mortars, similar to the average of twelve Seljuk bricks and brick mortar density and porosity values.

Tokat Gök Medrese

The bulk density and effective porosity values of tile mortar, body and repair mortars of Tokat Gök Medrese were shown in Table 4.3.

For the original materials, the average density of tile mortars (TTM) were 1, 24 ± 0.05 g/cm^3 and their average porosity was 44 ± 4%. The average density of tile bodies (TB) were 1.40 ± 0.01 g/cm^3 and their average porosity was 45 ± 0.4 %. The repair mortars of Tokat Gök Medrese had the average density values of 1.55±0.2. Their average porosity value was 26 ± 6.5 % as seen in Table 4.3.

Table 4.3 Bulk density and porosity values of tile mortar, tile body and repair mortars of Tokat Gök Medrese.

Tokat Gök Medrese							
	Original Materials		Repair Mortars				
	TTM Tile Mortar	**TB1** Tile Body	**TM1**	**TM2**	**TM3**	**TM4***	**TM5**
d (g/cm^3)	1.24 ± 0,05	1.40 ± 0,01	1.58 ± 0,08	1.47 ± 0.08	1.41 ± 0,1	1.87	1.44 ± 0
P (%)	44 ± 4	45 ± 0,4	21 ± 8	24 ± 8	35 ± 1	28	25 ± 5

*Only one piece was available

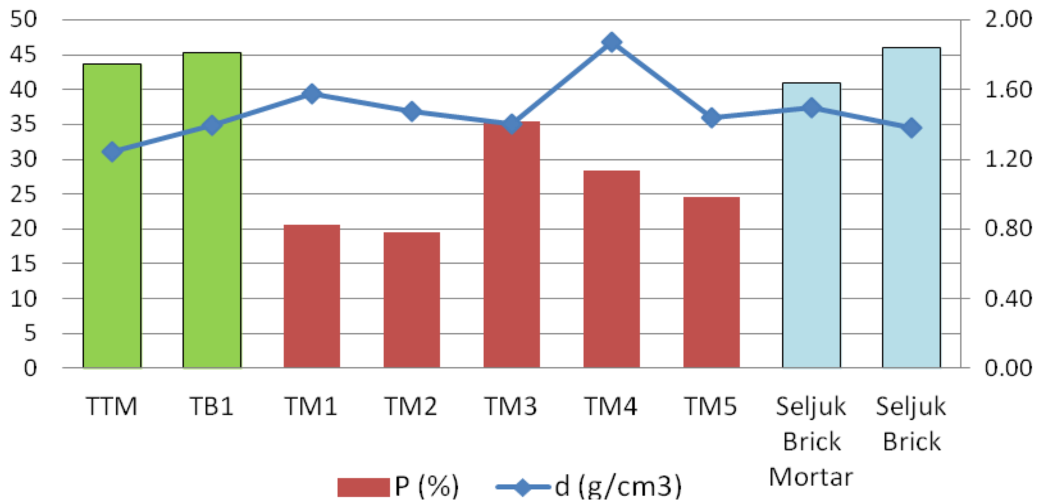


Figure 4.5 Bulk density and porosity values of Tokat Gök Medrese and their comparison with other Seljuk Monuments (Green; Tile Mortar and Body samples, Red; Mortar samples, Blue; Seljuk Period brick mortar and brick samples from Tunçoku, 2001).

According to the results, original tile bodies and tile mortars had quite similar lower bulk density and higher porosity than the repair mortars, similar to the average of twelve Seljuk bricks and brick mortar density and porosity values..

4.2 Modulus of Elasticity of Tile Bodies and Mortars (Young's Modulus)

Moduli of elasticity of mortar and tile body samples were determined by ultrasonic pulse velocity (UPV) and bulk density measurements. The samples were relatively deteriorated. Their pores might be contaminated with salt crystals which might quite affect the results. As shown in Table 4.4, E_{Mod} of Sivas Gök Medrese tile mortar samples had the average value of 4705±620 MPa. The tile bodies of Tokat Gök Medrese had the average value of 2547.4 ±888 MPa.

The obtained values of this study were compared with other Seljuk Period building mortars. They had average value of 1555.2 ±704 MPa (Tunçoku, 2001).

Table 4.4 U.P.V. and E_{Mod} values of tile mortar and body samples.

	Year	Sample Codes	U.P.V. (m/s)	E_{Mod} (MPa)
Sivas Gök Medrese Mortar Samples	1997	**SM1**	1840,2	4266,9
		SM2	2020,3	5143.1
Tokat Gök Medrese Tile Body Samples	1997	**TB3**	959,2	1288,2
		TB4	1425,9	2687,4
		TB5	1385,5	2846,6
	2010	**TB7**	1483.6	3367.4
Seljuk Period Building mortars				1555.2±704

4.3 Raw Materials Properties

4.3.1 Acid Soluble / Insoluble and Water Soluble / Insoluble Ratios of Tile Mortars

The binder-aggregate proportions of the mortars were determined by using the procedure of Middendorf et al (1998).

The results showed that the total binder was 97.6±0.04% and acid-insoluble aggregate was 2.4±0.00% for Sivas tile mortars. The similar results were observed for the tile mortar of Tokat Gök Medrese. The proportion of binder was 96.5±0.58% and the acid-insoluble aggregate was 3.5±0.6% as shown in Table 4.5.

Table 4.5 Acid and water soluble and insoluble proportions of Tokat and Sivas Gök Medrese tile mortars

	Acid Soluble (%)	**Acid Insoluble (%)**	**Water Soluble (%)**	**Water Insoluble (%)**	**Calcite Contents (%)**
STM	97.6±0.1	2.4±0.0	93.1	6.9	4.5±0.0
TTM	96.5±0.6	3.5±0.6	91.9	8.1	4.6±0.6

The gypsum in the tile mortar was completely dissolved in water. The results showed that the water-insoluble part was 6.9% in Sivas tile mortars. The similar results were observed for the tile mortars of Tokat Gök Medrese. The proportion of water-insoluble part was 8.1 % as shown in Table 4.5.

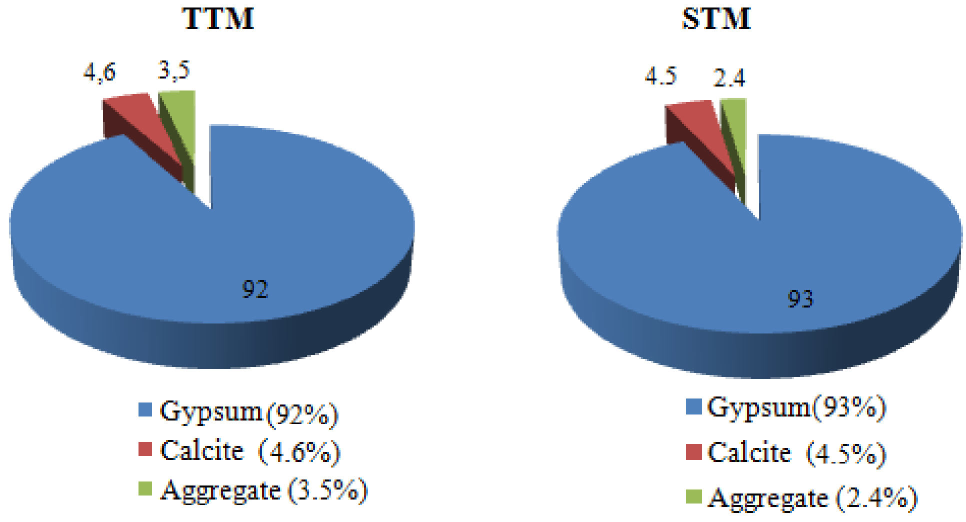


Figure 4.6. The components of acid and water insoluble parts of tile mortars and their percentages (TTM: Tokat Tile Mortar, STM: Sivas Tile Mortar)

Figure 4.6 summarizes the main components of tile mortars. The water soluble parts were gypsum, the difference between weter-insoluble and acid-insoluble part was calcite and the remainings were the aggregates of tile mortars.

4.3.2 Particle Size Distributions of the Tile Mortar Aggregates

Acid-insoluble aggregates were and drying-oven dried. Their size distribution was made by standard sieve analysis by using 2000, 1000, 500, 250, 125 and 75 μm sieves. The results were plotted in Figure 4.7 as mass percentage (%) of particle size (μm).

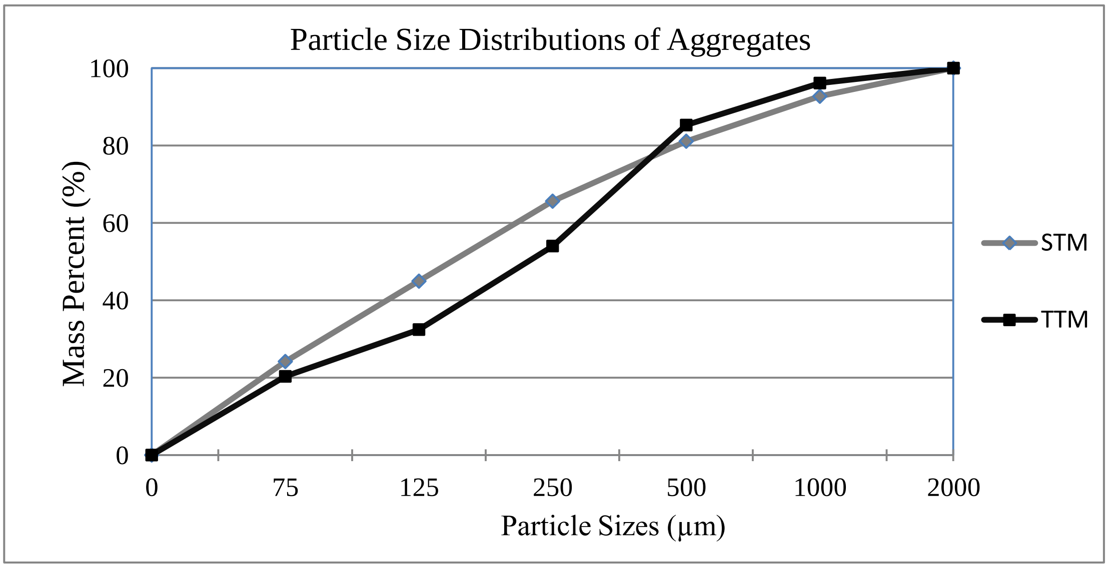
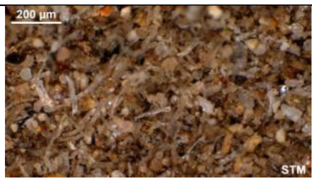
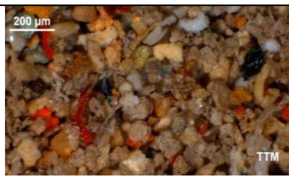
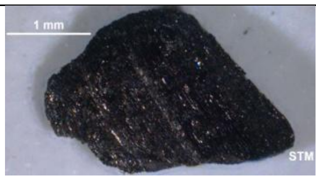


Figure 4.7 Particle size distribution of the aggregates in tile mortar samples (STM: Sivas Gök Medrese Tile Mortar, TTM: Tokat Gök Medrese Tile Mortar)

The aggregates were examined by a stereomicroscope and photographed. According those observations, the aggregates contained some tile fragments with their glazes (Table 4.6). Visual differences were observed for the aggregates of Sivas Gök Medrese and Tokat Gök Medrese mortars.

Table 4.6. The photographs of aggregates in Tokat Gök Medrese and Sivas Gik Medrese (scales were from Tucker, 2001)

Mesh Sizes	**Particle distributions of STM Aggregates**	**Particle distributions of TTM Aggregates**
<75 µm (Sand-Silt-Clay)		
>75 µm (Sand)		
>125 µm (Sand)		
>250 µm (Sand)		
>500 µm (Sand)		
>1000 µm (Sand)		
>2000 µm (Granule)		

4.3.3 Pore Size Distribution of Tile Bodies and the Mortars

Pore size distribution of tile body and mortar samples were conducted by measurements using mercury porosimeter. They were then compared with the pore size distribution of the poultices from literature that were used to extract soluble salts from porous building materials.

The results have shown that tile body (TT) had pores ranging between 5.2 μm and 74 μm (Figure 4.8). The tile mortar (TTM) had pore diameters ranging between 0.0025 μm to 5.9 μm, 5.9 μm to 18.7 μm and 32.4 μm to 211.1 μm (Figure 4.9). In additon, TM3 had pore sizes ranging between 0.0071 μm to 0.0087 μm and 1.3 μm to 31.9 μm (Figure 4.10).

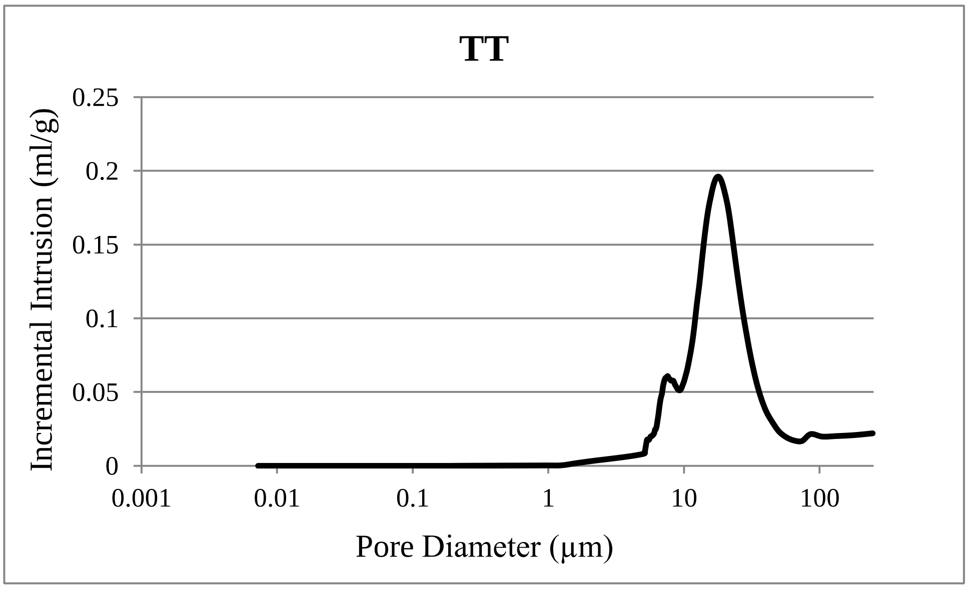


Figure 4.8. Pore size distribution of Tokat Gök Medrese tile body (TT)

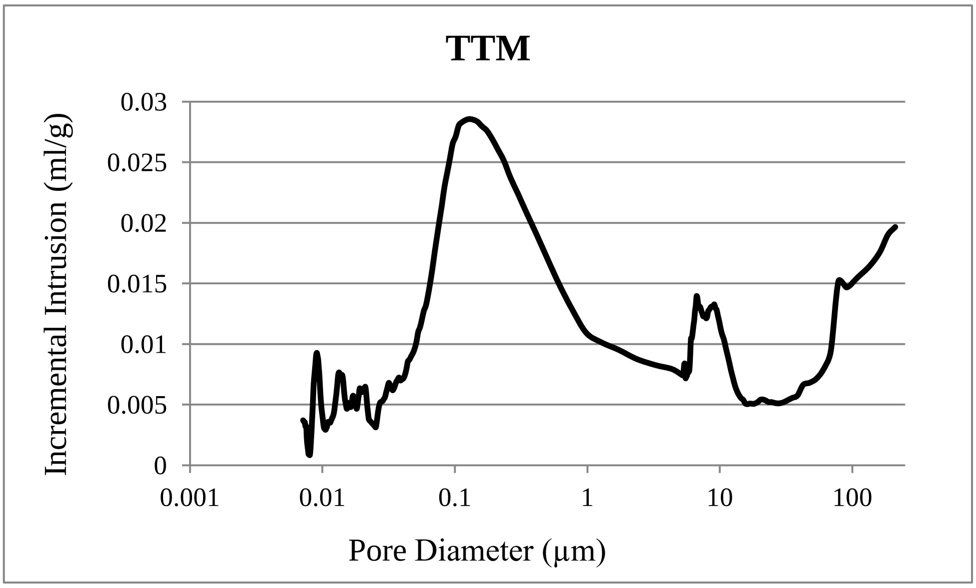


Figure 4.9 Pore size distribution of Tokat Gök Medrese tile mortar (TTM)

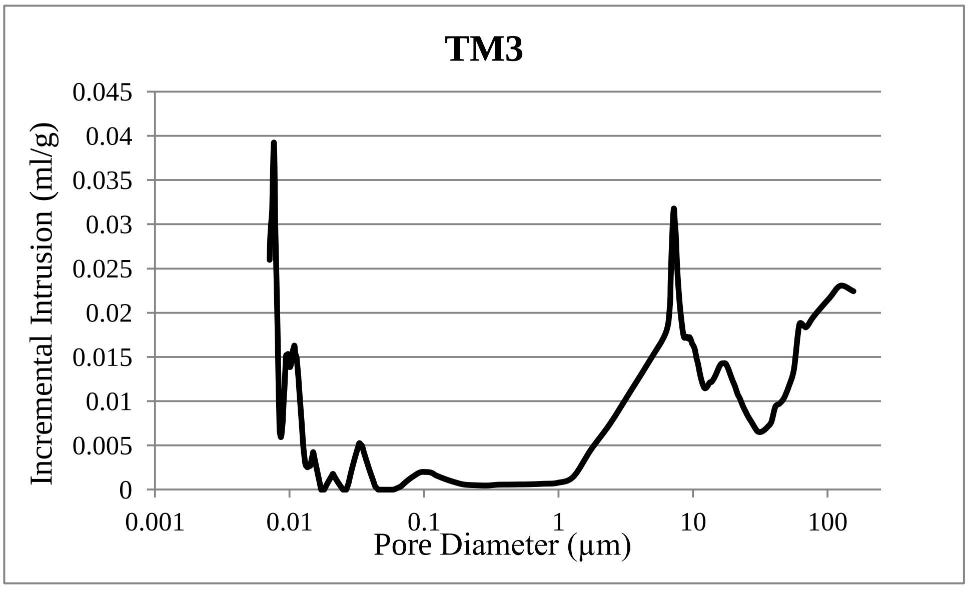


Figure 4.10. Pore size distribution of Tokat Gök Medrese mortar sample (TM3)

The pore size distribution of glazed brick body (SGB) had shown that pore sizes were between 0.021 µm to 6.7 µm and 32.8 µm to 173.2 µm (Figure 4.11). The tile mortar (STM) had pore diameters ranging between 1.2 µm to 40.2 µm for Sivas Gök Medrese (Figure 4.12).

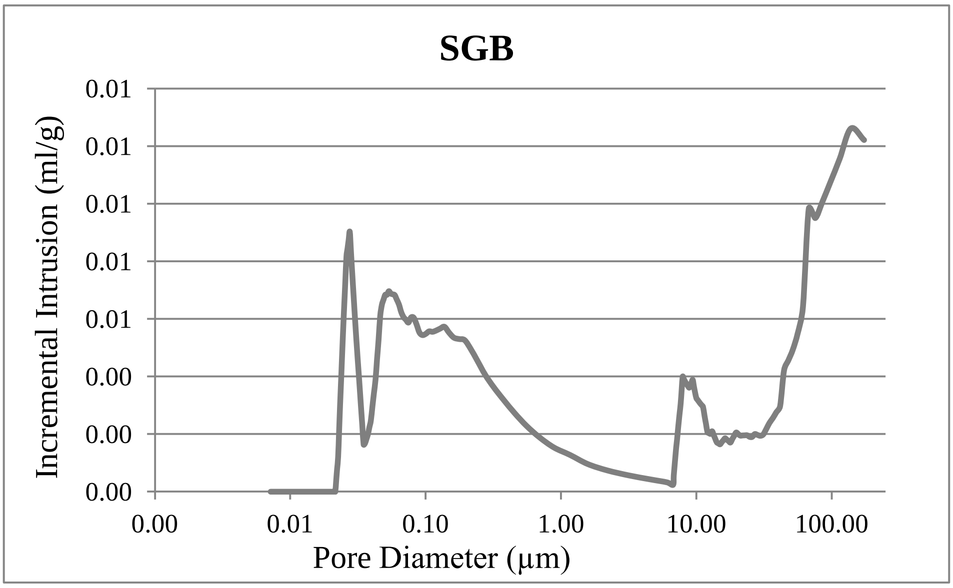


Figure 4.11. Pore size distribution of Sivas Gök Medrese glazed brick body (SGB) (from laboratory archive)

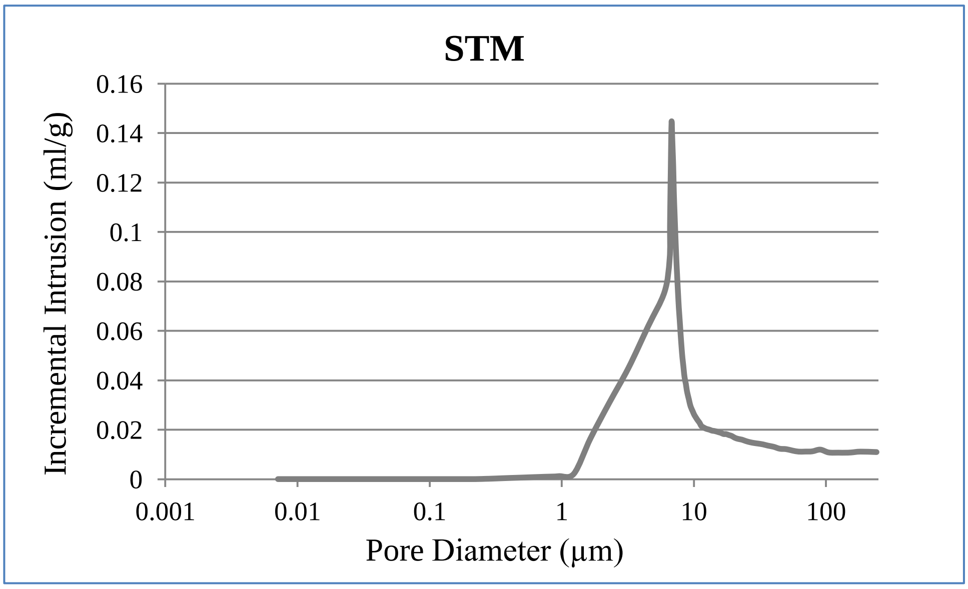


Figure 4.12. Pore size distribution of Sivas Gök Medrese tile mortar (STM)

The ranges of values are summarized in Figure 4.13 below for comparison.

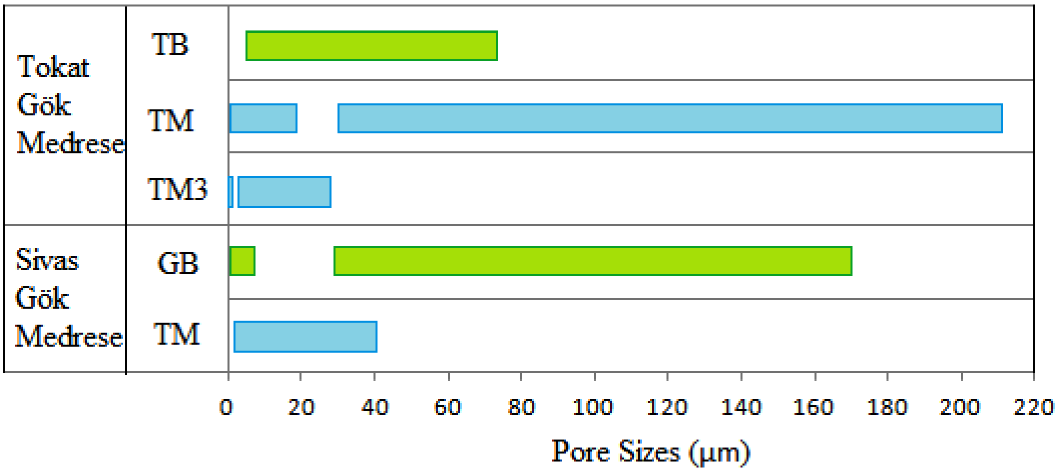


Figure 4.13 Comparison of the pore size distributions of tile bodies and the mortars of Tokat Gök Medrese and Sivas Gök Medreses (TB: Tile Body, TM: Tile Mortar, GB: Glazed Brick)

4.3.4 Pozzolanic Activity of Tile Bodies and Brick Samples

According to the pozzolanic activity measurements, it was seen in Table 4.7 that the conductivities of brick samples of Sivas Gök Medrese were 29.32 (SBr1) and 26.76 mS/cm (SBr2). The conductivity of tile body was 1.51 mS/cm (SB). Moreover, the conductivities of brick samples of Tokat Gök Medrese were 22.31 (TBr1) and 6.61 mS/cm (TBr2) and the tile body 3.06 mS/cm (TB).

In the experiments, it was assumed that the materials had the same granular sizes and surface area. Pozzolanic activities of tile body and brick samples were good and high (Luxan et al, 1989).

Table 4.7 Pozzolanic activities of tile body and brick samples

	Sample Codes	Conductiviy (mS/cm)	Evalaution According to Luxan et al (1989)
Sivas Gök Medrese	**SB** - Tile Body	1.51	**Good Pozzolanicity** (for the values higher than 1.2mS/cm)
	SBr1 - Brick	29.32	
	SBr2 -Powdered Brick	26.76	
Tokat Gök Medrese	**TB** -Tile Body	3.06	
	TBr1 - Brick	22.31	
	TBr2 -Powdered Brick	6.61	

4.3.5 Oil, Hydrolysable Resins and Proteins in Tile Mortars

The procedure was applied for tile mortars of both monuments. STM and TTM gave positive results to the oil and hydrolysable resins. But it was negative for the proteins and –CO-NH groups. Those spot tests were not considered to be sensitive to indicate the presence of oil and resins in tile mortars and the organic additives might change their forms in time.

4.4 Petrographic Analyses

4.4.1 Cross Section and Thin Section Analysis

4.4.1.1 Cross Sections

Precise numerical data was obtained about the thickness of the glaze (0.026mm) on the surface of the body of polished cross sections of tile fragments (Figure 4.14) through microscopic examination.

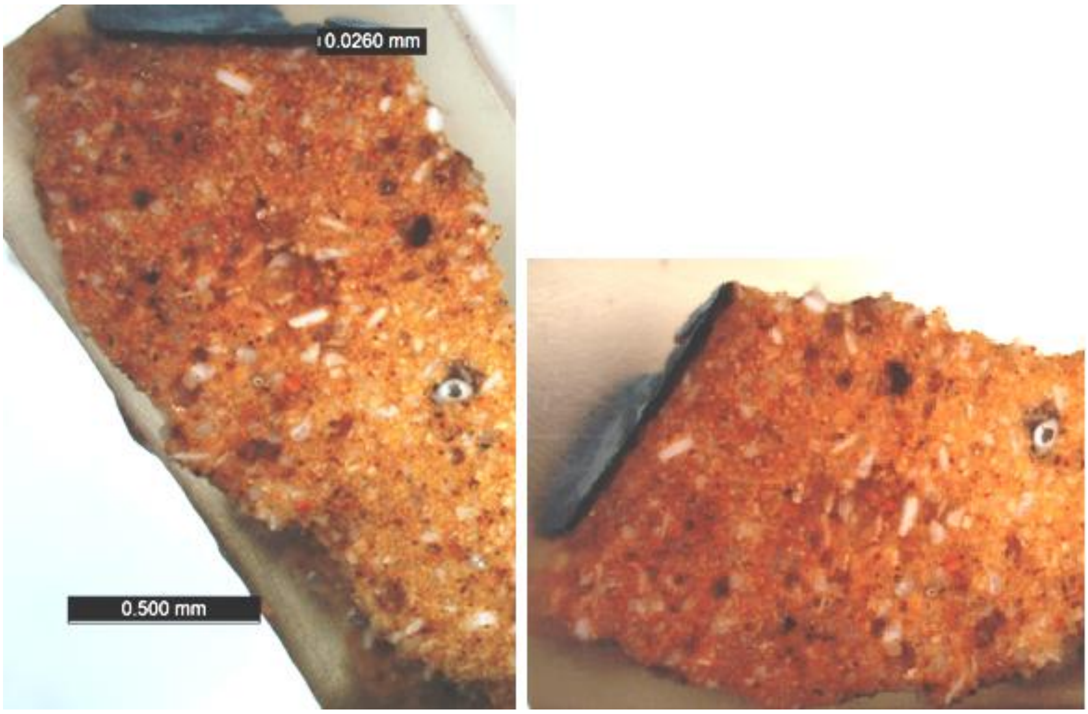


Figure 4.14 Tokat Gök Medrese tile body and its eggplant purple glaze. The thickness was 0.026 mm

In Figure 4.15, it was seen the interaction of tile body with its mortar was well and mortar surrounded the body.

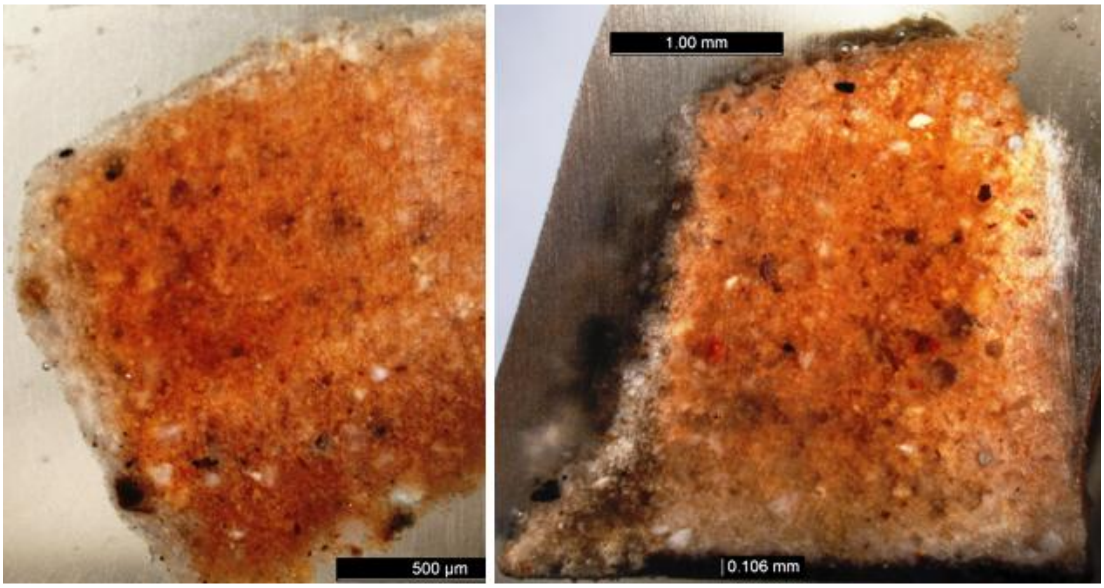


Figure 4.15 Sivas Gök Medrese tile body which was well connected with its mortar

The image analysis of mortars was tried to be done with Leica Application Suite software. In the method, quantitative analysis of white lumps was done. The visible white lumps were drawn to determine their total amount in the mixture (Figure 4.16). According to the manual calculations, white lumps were about 7% of the total area.

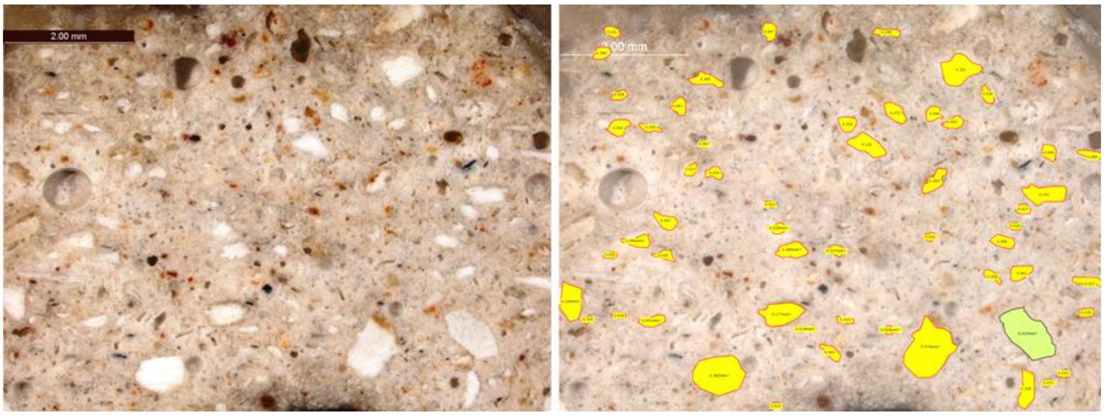


Figure 4.16 Cross Sections of mortar samples of Sivas Gök Medrese (STM)

The cross sections of recent repair mortars were also documented with photographs. The mortar SRM2 was generally used as infill material in the lost parts of brick and SRM1 was used on the lost parts of tiles on the wall.

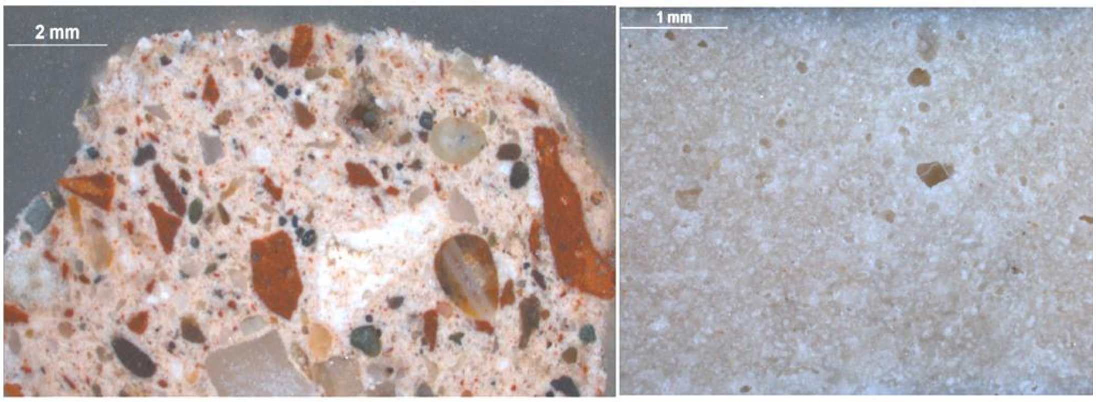


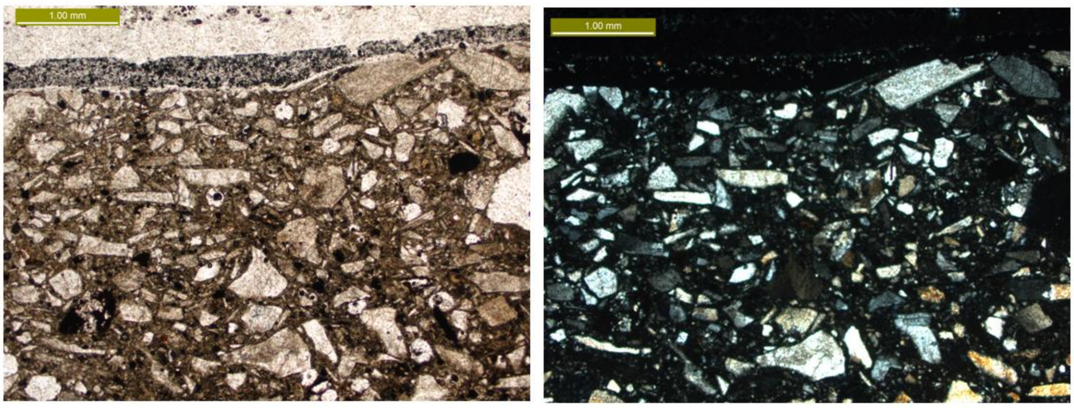
Figure 4.17 Cross sections of tile and mortar samples of Sivas Gök Medrese SRM2 (left side) and SRM1 (right side-Hydraulic Based Lime Mortar)

4.4.1.2 Thin Sections

The study of the thin sections of the tile body gave clues about the mineralogical and petrographical properties of the samples.

In the thin section of Tokat Gök Medrese tile body (TB), the mineral grains were mainly coarse quartz crystals and feldspars which were about 500 microns in size. Metamorphic rock fragments were also seen. Coarse quartz crystals were added as temper, since they had angular shapes. Quartz and plagioclase minerals were the major minerals observed in the thin section of the tile body (TB) (Figure 4.18). Some schist fragments composed of opacified biotites and quartz were observed. Limonitized opaque minerals were present. There were also some micro and crypto crystalline rock fragments.

Matrix of the tile body was composed of isotropic materials (such as vitrified glass) with plagioclase iron (II) oxide and hydroxides and clays as opaque minerals (Figure 4.19).



(a) (b)

Figure 4.18 Tile body and their glazes of Tokat Gök Medrese (TB). (a) Single and (b) Cross nicols

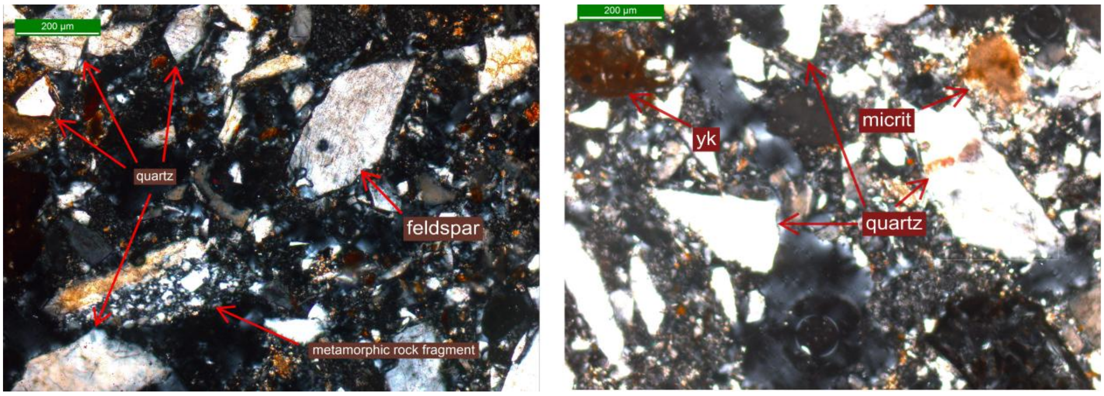


Figure 4.19 Thin section images of tile body sample of Tokat Gök Medrese. Cross nicols (Quartz, Feldspar, Micrit and Metamorphic rock fragments (yk))

The thin section images of Sivas Gök Medrese glazed brick sample (SGB) proved the presence of angular and sub-angular shapes of large quartz grains which were added as temper. There were mainly polycrystalline quartz minerals with mica crystals, plagioclase feldspars, biotite as mica crystals and plenty of hematite were observed. In the matrix of the brick, micritic calcite crystals were present (Figure 4.20).

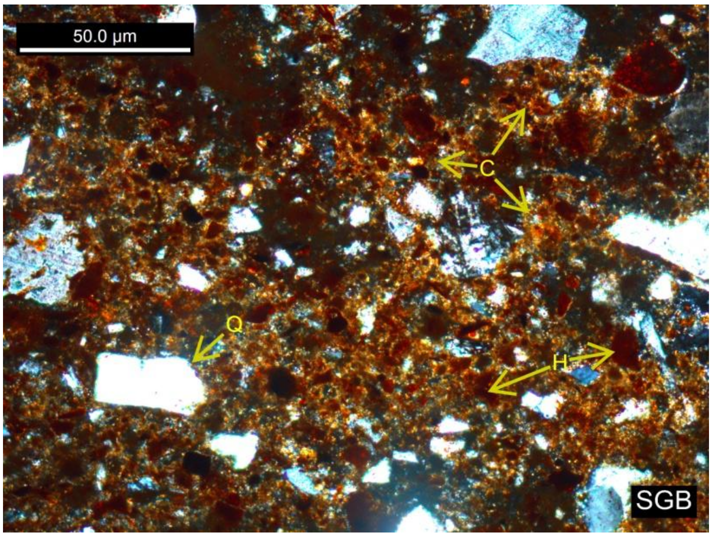


Figure 4.20 Thin section images of a glazed brick, Sivas Gök Medrese. Cross Nicol. (C: Calcite, Q: Quartz, H: Hematite)

The thin sections of tile mortars were analysed for both of the medreses. Their mineral types, differences and similarities were outlined. Sivas Gök Medrese tile mortar sample (STM) had mainly gypsum minerals with micro and macro crystals. Calcite crystals were also detected as micritic calcite lumps. Quartz crystals with varying sizes and brick fragments were rarely detected. Black colored charcoal or coal fragments were detected in the sample (Figure 4.21).

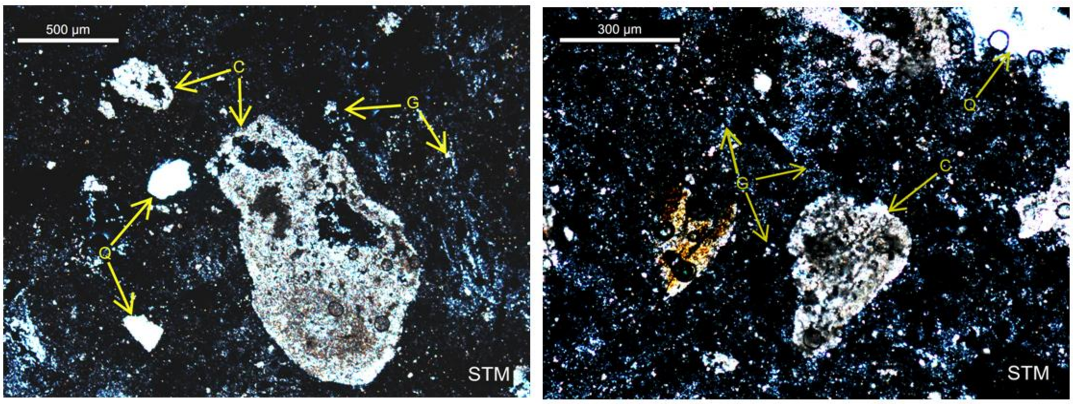


Figure 4.21 Thin section images of tile mortar, Sivas Gök Medrese. Cross nicols. (G:Gypsum, Q:Quartz, C: Calcite)

Tokat Gök Medrese tile mortar samples (TTM) had mainly gypsum minerals mainly as micro crystals. Calcite crystals were detected together with quartz crystals in varying sizes and brick fragments rarely observed in the mortar. Black colored charcoal or coal fragments were also detected in the sampless (Figure 4.22).

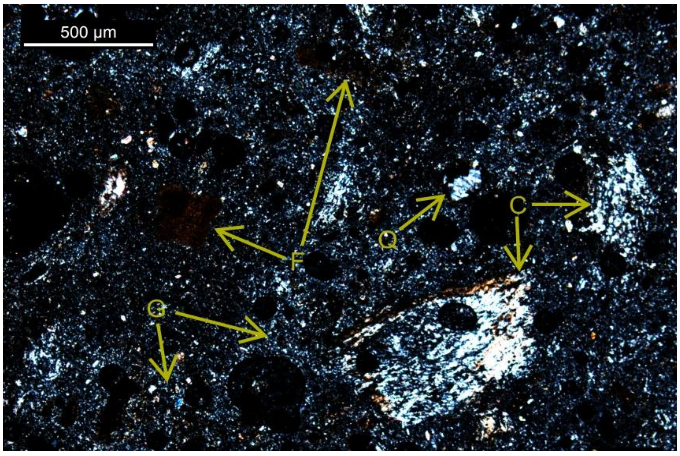


Figure 4.22 Thin section images of tile mortar, Tokat Gök Medrese. Cross nicols. (G:Gypsum, Q:Quartz, C: Calcite, F: Feldspar)

4.4.2 XRD Analyses

Tile Bodies

The XRD analyses were carried out with the powdered tile bodies. XRD traces of tile bodies showed that the main mineral was quartz. A small amount of feldspar was detected in Tokat tile body (TB) but it was not detected in Sivas tile body (TB) (Figure 4.23) in XRD traces.

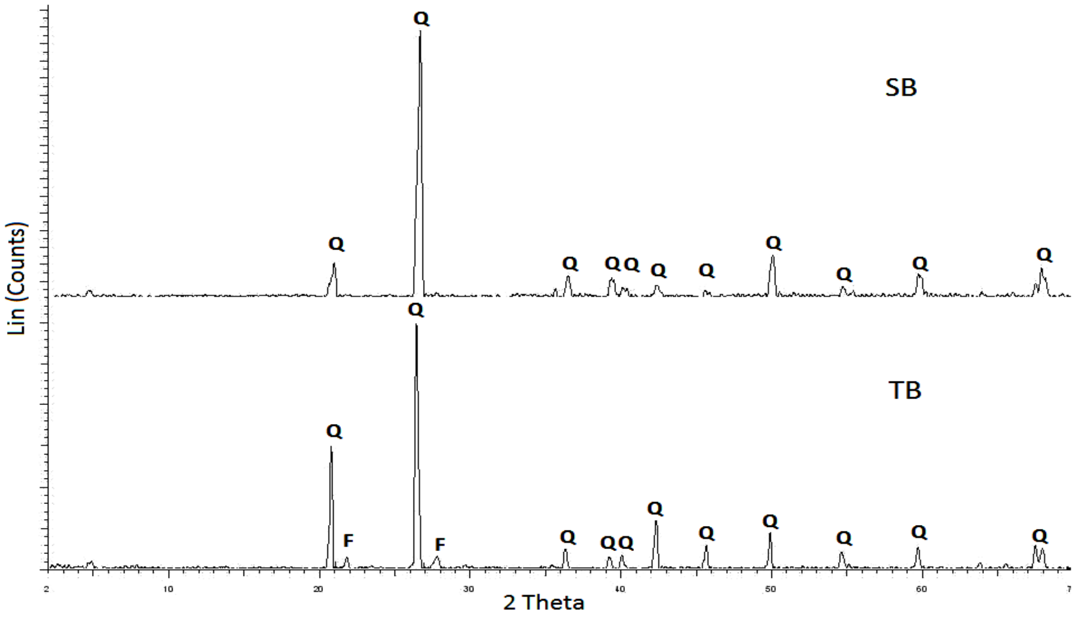


Figure 4.23 XRD traces of tile bodies as Sivas Gökmedrese (SB) and Tokat Gökmedrese (TB) Q: Quartz F: Feldspar

Glazes

The XRD traces of the glazes contained quartz, feldspar and cassiterite minerals as shown in Figure 4.24.

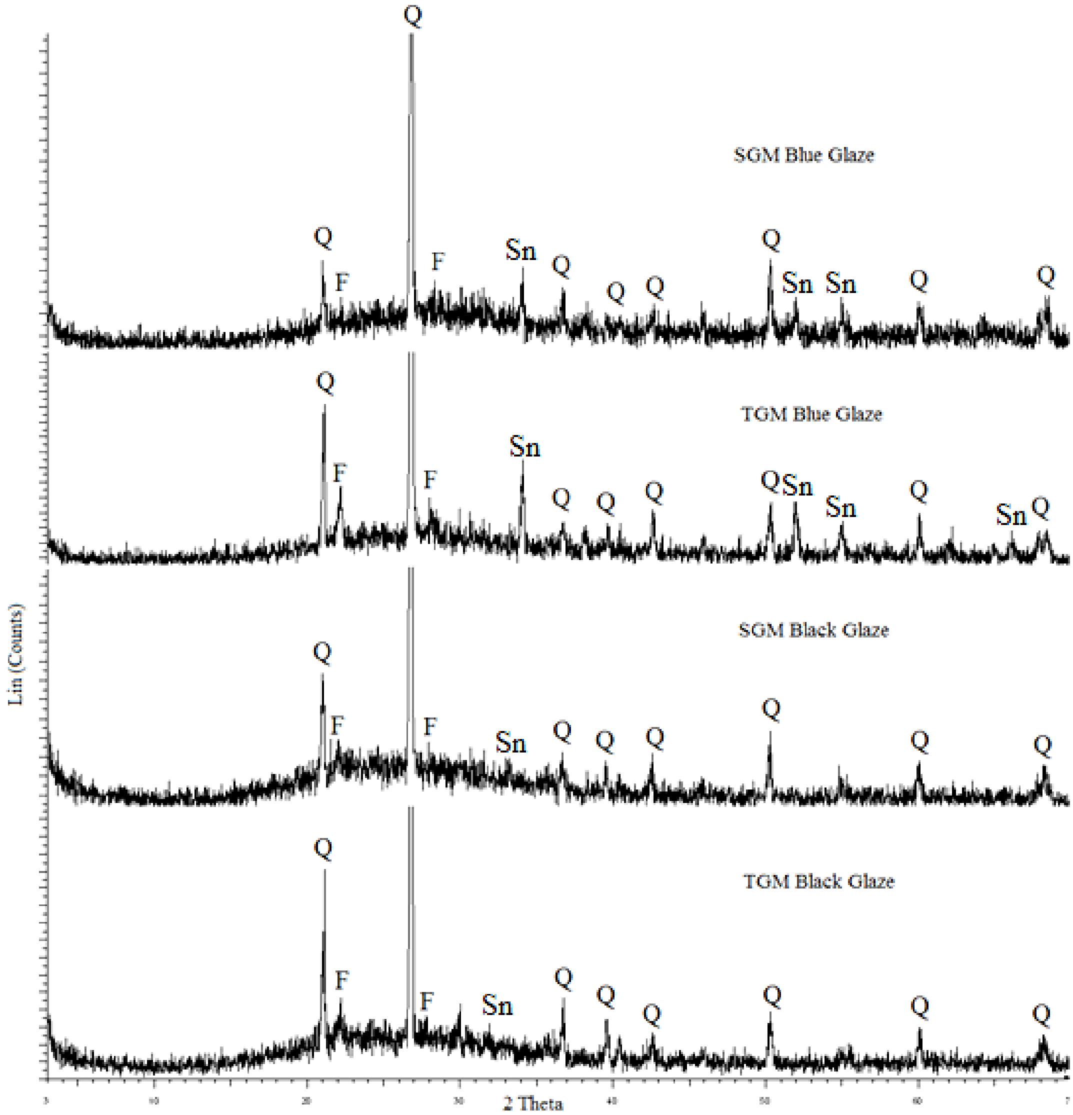


Figure 4.24. XRD traces of glazes: Q: Quartz, F: Feldspar; Sn: Cassiterite (SnO_2), SGM: Sivas Gök Medrese, TGM: Tokat Gök Medrese

Tile Mortars

The XRD traces of powdered tile mortar samples indicated that the main mineral was gypsum as binder for both of the mortar samples (Figure 4.25).

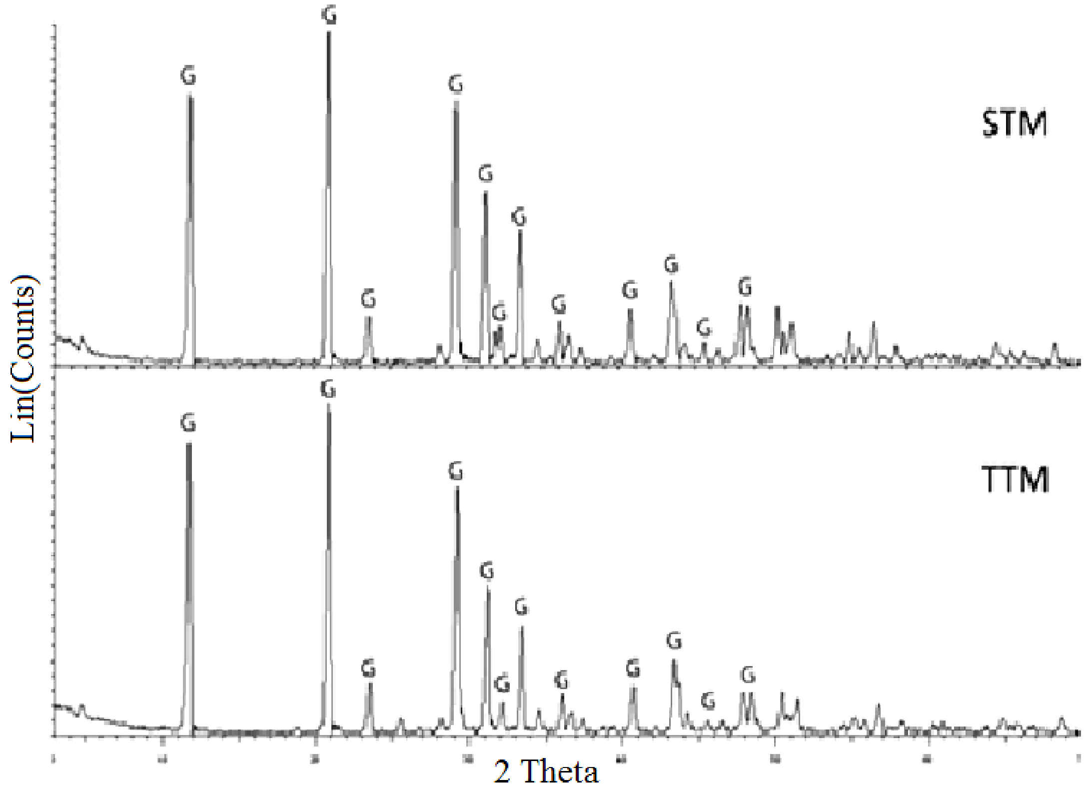


Figure 4.25 XRD traces of some Sivas Gökmedrese (STM) and Tokat Gökmedrese (TTM) tile mortars G: Gypsum

Aggregate minerals were not clearly seen in XRD traces. In order to detect aggregate minerals, additional studies were done to separate aggregates as expressed in sections 4.3.1 and 4.3.2. The aggregates which were smaller than 75 μm were analyzed with XRD. According to the XRD analyses, quartz was the main mineral for both of the aggregate samples which were smaller than 75 μm. Feldspar and hematite were also seen in the traces (Figure 4.26).

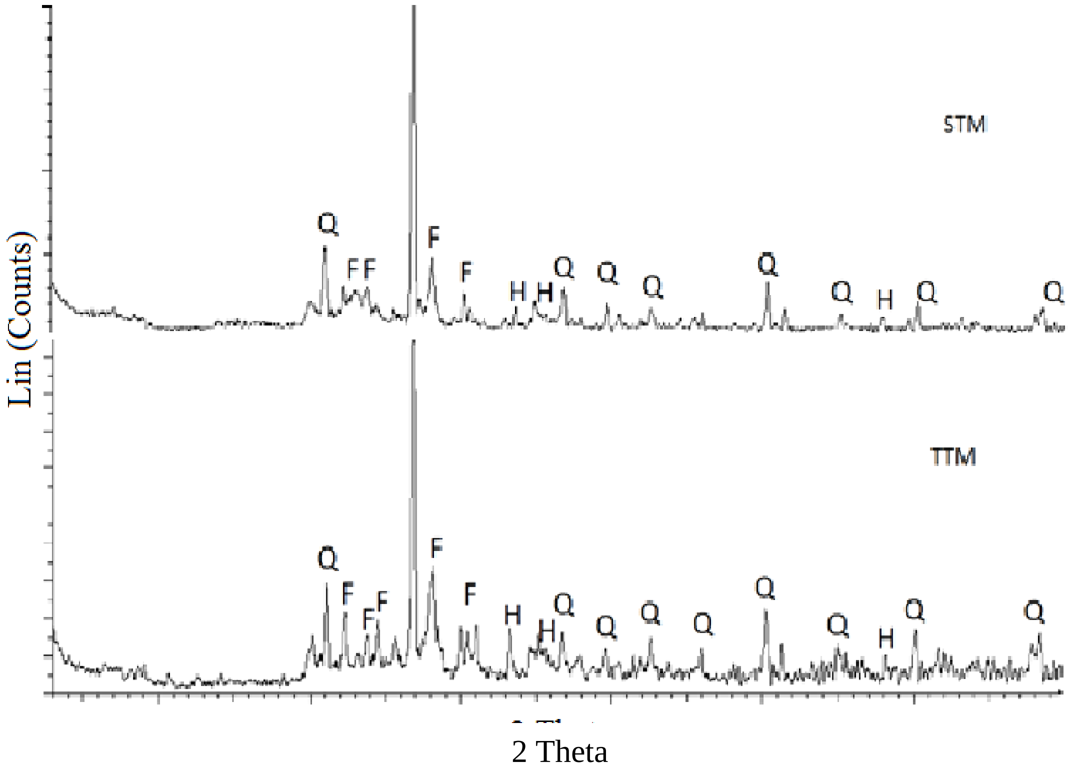


Figure 4.26 XRD traces of the aggregates of Sivas Gök Medrese (STM) and Tokat Gök Medrese (TTM) tile mortars which were smaller than 75 µm. Q: Quartz, F: Feldspar, H: Hematite

The presence of calcite in tile mortars was detected from the water-insoluble residues of both of the mortars. Due to their small amounts, they could not be detected before dissolving gypsum in water (Figure 4.27). According to the XRD results, calcite, quartz and feldspars were the main components of the water-insoluble aggregates. The additional study was done to detect the amount of calcite for both STM and TTM samples.

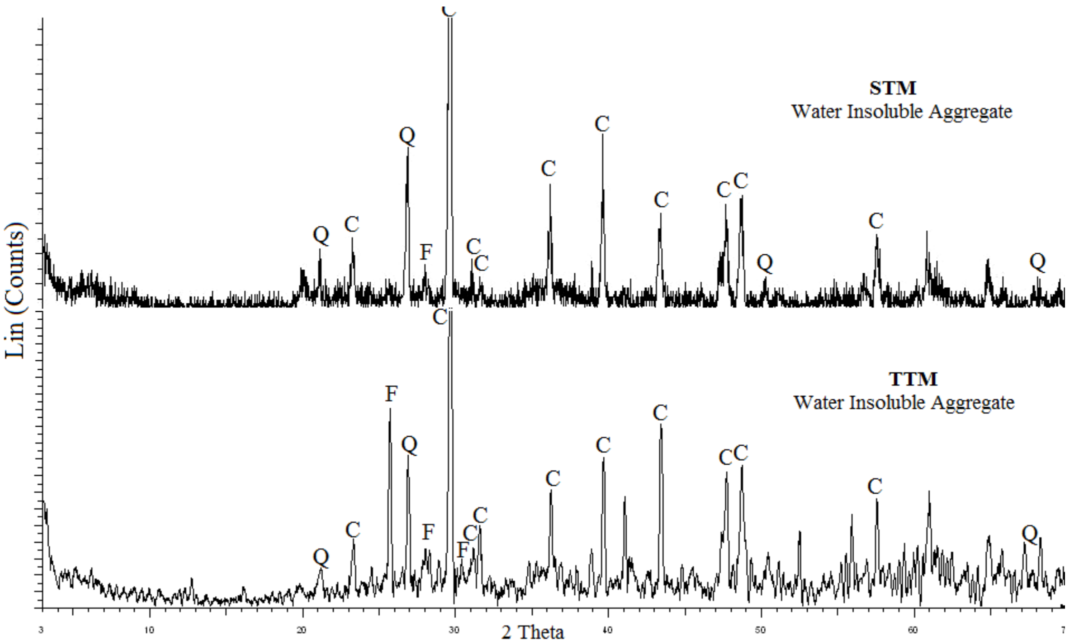


Figure 4.27 XRD traces of water insoluble aggregates of STM (Sivas Gök Medrese Tile Mortar) and TTM (Tokat Gök Medrese Tile Mortars) C: Calcite, Q: Quartz, F: Feldspar

The tile mortars had gypsum lumps which were seen by eye or with the photographs of stereomicroscope. The qualitative analysis of the lumps was done with XRD analysis after removing them with mechanical methods. The analysis had shown that those lumps were composed of gypsum. No other peaks were observed other than gypsum (Figure 4.28).

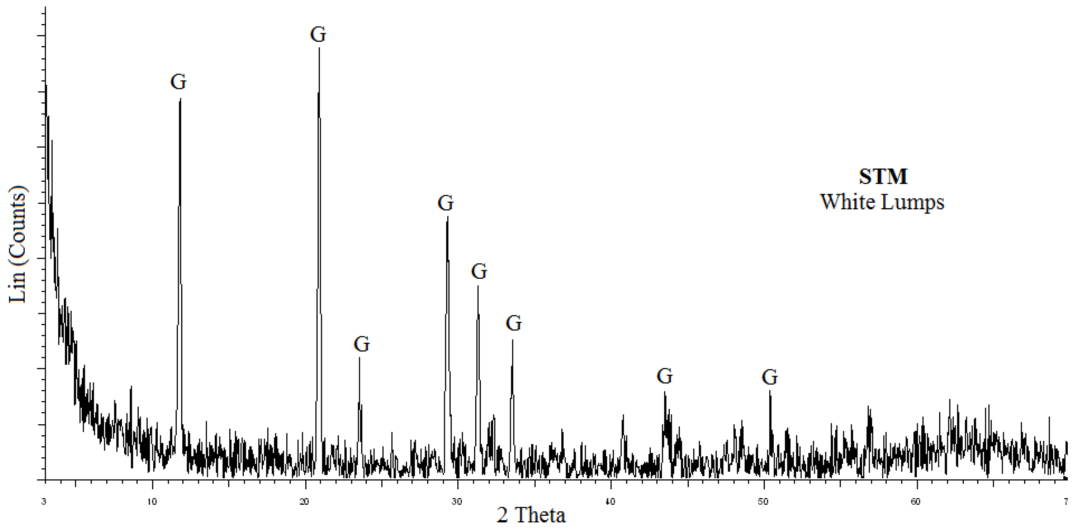


Figure 4.28 XRD Traces of White Lumps of STM G: Gypsum

Some small pieces of mortars were collected from the main eyvan façade of Tokat Gök Medrese. Those mortars were behind the tiles which were mainly lost. Some repair mortars were applied there and a black patina on the mortars made them difficult to distinguish from the original ones.

The XRD traces of the mortars were given in Figure 4.29 showing the mineral compositions of TM1, TM2, TM3, TM4 and TM5. The main mineral was determined to be gypsum except from TM4. Calcite was main mineral in its composition. In addition to calcite, quartz, gypsum and feldspar minerals were found to exist in its composition.

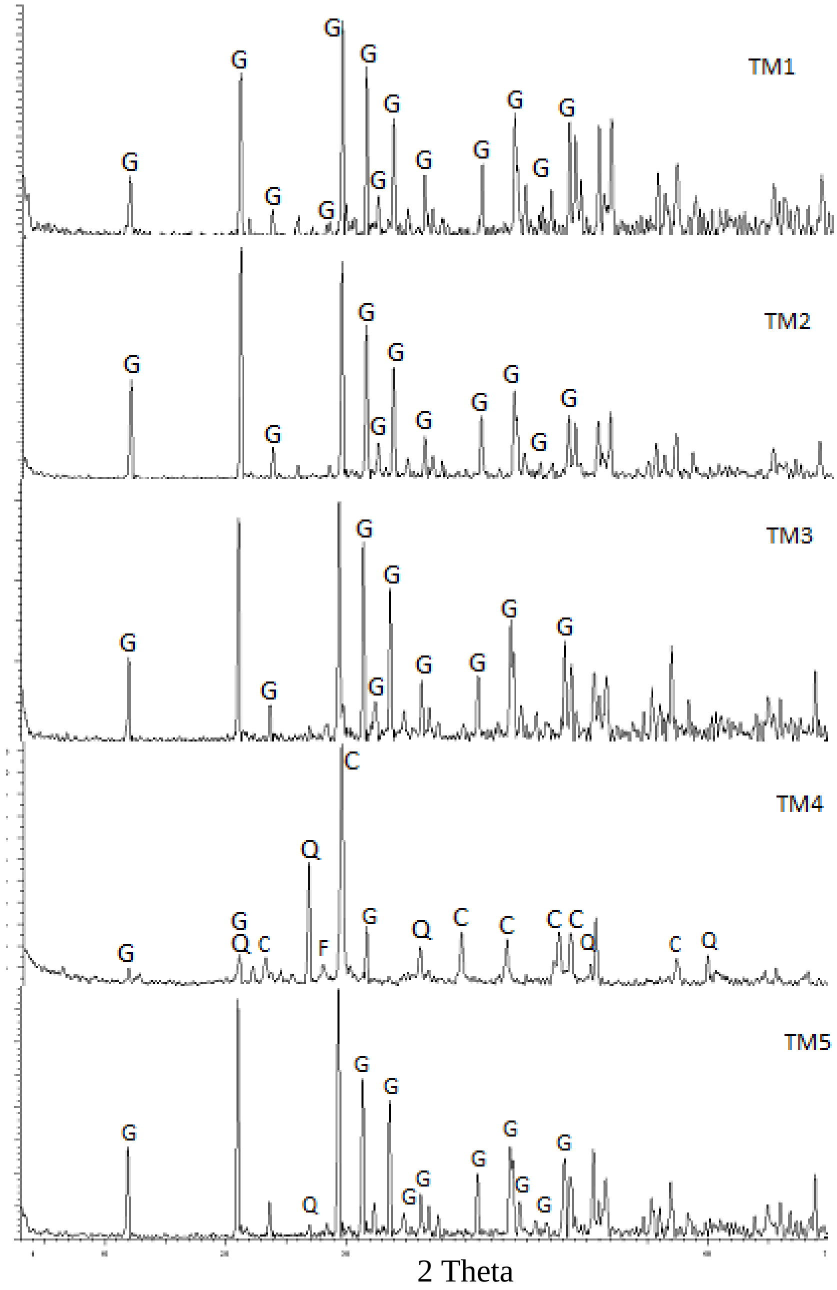


Figure 4.29 XRD traces of mortars from the main eyvan façade of Tokat Gök Medrese G: Gypsum, Q: Quartz, C: Calcite

4.4.3 SEM-EDX Analyses

SEM images and EDX analyses were performed on the tile mortars. It was aimed to determine the pore morphology and chemical compositions.

The Figure 4.30 and the Figure 4.31 were the SEM images of gypsum based mortar. Those figures showed the presence of pores less than 500µ in size.

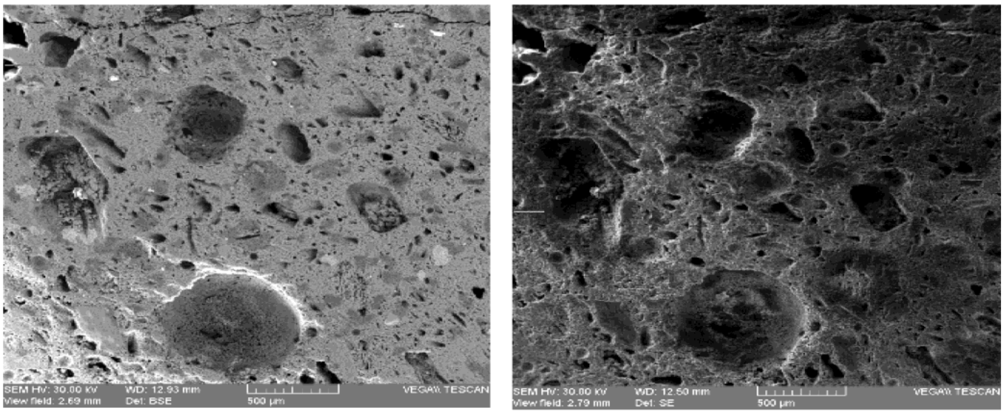


Figure 4.30 SEM view of the gypsum based tile mortar (a) SE and (b) BSE images of STM

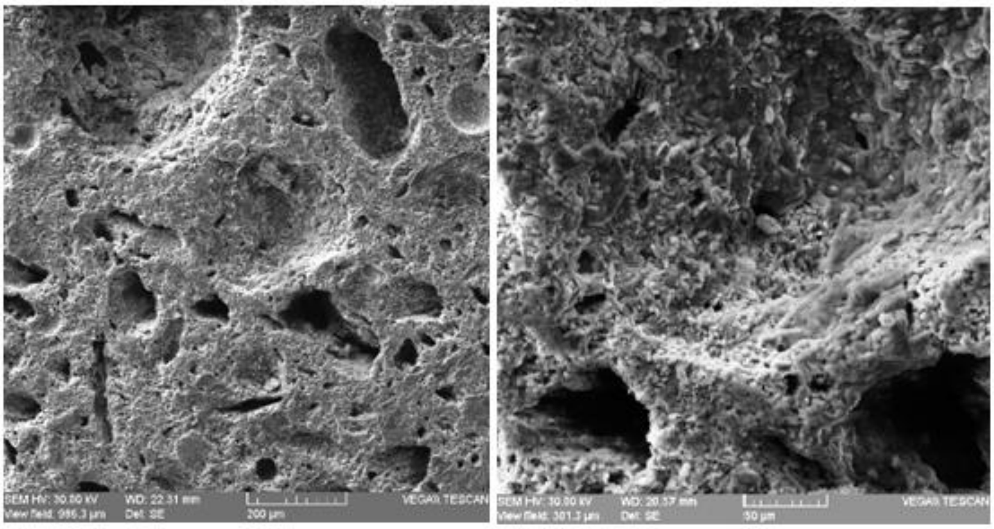


Figure 4.31 SEM view of the gypsum based tile mortar-SE images of STM

4.5 Qualitative and Quantitative Analysis of Salts

4.5.1 Quantitative Analysis

Conductivity measurement of salts

The quantitative analyses of soluble salt content of the brick, tile body and mortar samples were done by using a conductometer. Samples were classified and evaluated according to their collection years.

The tile body samples belonging to 1997 had relatively lower salt contents except STM*. Their salt content were between 0.4 to 4.5 %. For the tile bodies of Sivas Gök Medrese, the average salt contents calculated from conductivity measurements were 1.1±1 %. For the tile bodies of Tokat Gök Medrese, the average values were 3.4±1.6 %. The mortar sample STM was the most deteriorated part of the mortar in the powdered form. Salt content calculated from conductivity was 10%.

The brick, mortar and recent repair mortar samples belonging to 2010 had relatively higher salt contents. They were ranging between 3.0 to 11.5 %. For the materials of Sivas Gök Medrese, the average salt contents calculated from the conductivity were 8.71±1.2 %. For the mortars of Tokat Gök Medrese, the average salt contents were 7.6±3.2 % (Table 4.8).

Table 4.8 Conductivity test results of samples collected in 1997 and 2010; showing the amount of salts as percentages.

	1997 Sample Codes	**Amount of Salt (%) (Conductivity)**	**2010 Sample Codes**	**Amount of Salt (%) (Conductivity)**
Sivas G.M.	**SB**	1.8	**SBr2**	7.8
	SB2	0.4	**SRM1**	9.5
	STM*	10		
Tokat G.M.	**TB1**	2.3	**TBr1**	11.5
	TB2	4.5	**TBr2**	5.4

Table 4.8(Continued)

		TM1	3.9
		TM2	6.8
		TM3	6.5
		TM4	3.0
		TM5	10.2
		TB7**	10.1

* The mortar sample STM was in powdered form in its storage box. It was from the laboratory archive.
** It was a deposit on the tile body of TB7.

4.5.2 Qualitative Analysis

4.5.2.1 Ions with Spot Tests

Spot chemical analysis was done for the general definitions of salts. It was aimed to determine the presence of PO_4^{-2}, SO_4^{-2}, Cl^-, NO_2^-, NO_3^-, and CO_3^{-2} anions in the samples. Results were given in the table below.

Sivas Gök Medrese

The pink color of Figure 4.32 proved the existence of NO_3^- ions. In some cases the color was darker or lighter which was proportional to the amount of NO_3^- ions. For instance, the pink color of SS3, SS4, and SS6 was not as intense as the others.

All the salt samples from the south eyvan wall had SO_4^{-2}, NO_3^- and CO_3^{-2} ions. In addition, SS1 had Cl^- ion which was different from the other samples. The repair mortars (SRM1 and SRM2) had more anion types such as SO_4^{-2}, NO_2^- and NO_3^-. In addition, SRM1 had CO_3^{-2} and SRM2 had Cl^- ions. SBr2 was the only original mortar in the spot test experiment. It contained NO_2^-, NO_3^-, CO_3^{-2} and Cl^- ions (Table 4.9).

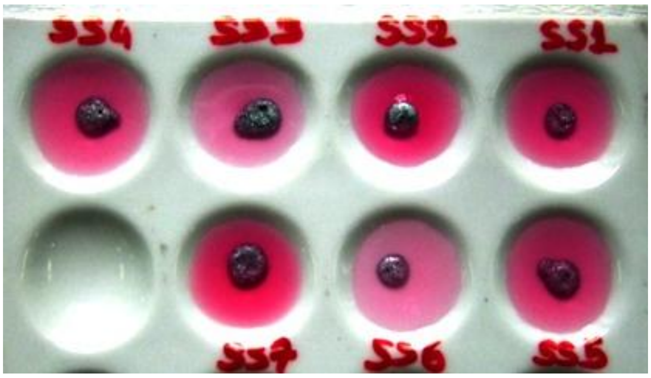


Figure 4.32 Spot test of salts which were directly taken from efflorescence zone in south eyvan façade of Sivas Gök Medrese proving the existence of NO_3^- as pink color

Tokat Gök Medrese

All the mortar samples of Tokat Gök Medrese had Cl^-, NO_3^- ions. They had PO_4^{-2} ion except TM4. CO_3^{-2} ion was only present in TM3 as shown in Table 4.10. The experiments were also performed with original and restoration materials such as bricks and repair mortars. They were also shown in Table 4.10

The XRD analyses were done to identify the salt minerals. To find the type of salt, spot tests were used to support the XRD results.

4.5.2.2 XRD Results of Salts

The brick samples containing salts and the salt samples from south eyvan wall of Sivas Gök Medrese were analyzed with XRD. Brick samples were analyzed before and after washing with distilled water (SBr2, TBr2) to detect the salts. Salts were examined both on salts which was taken directly on the eyvan walls of Sivas Gök Medrese where it was covered with new restoration materials.

The Figure 4.33 included the XRD traces of salt samples from Sivas Gök Medrese.

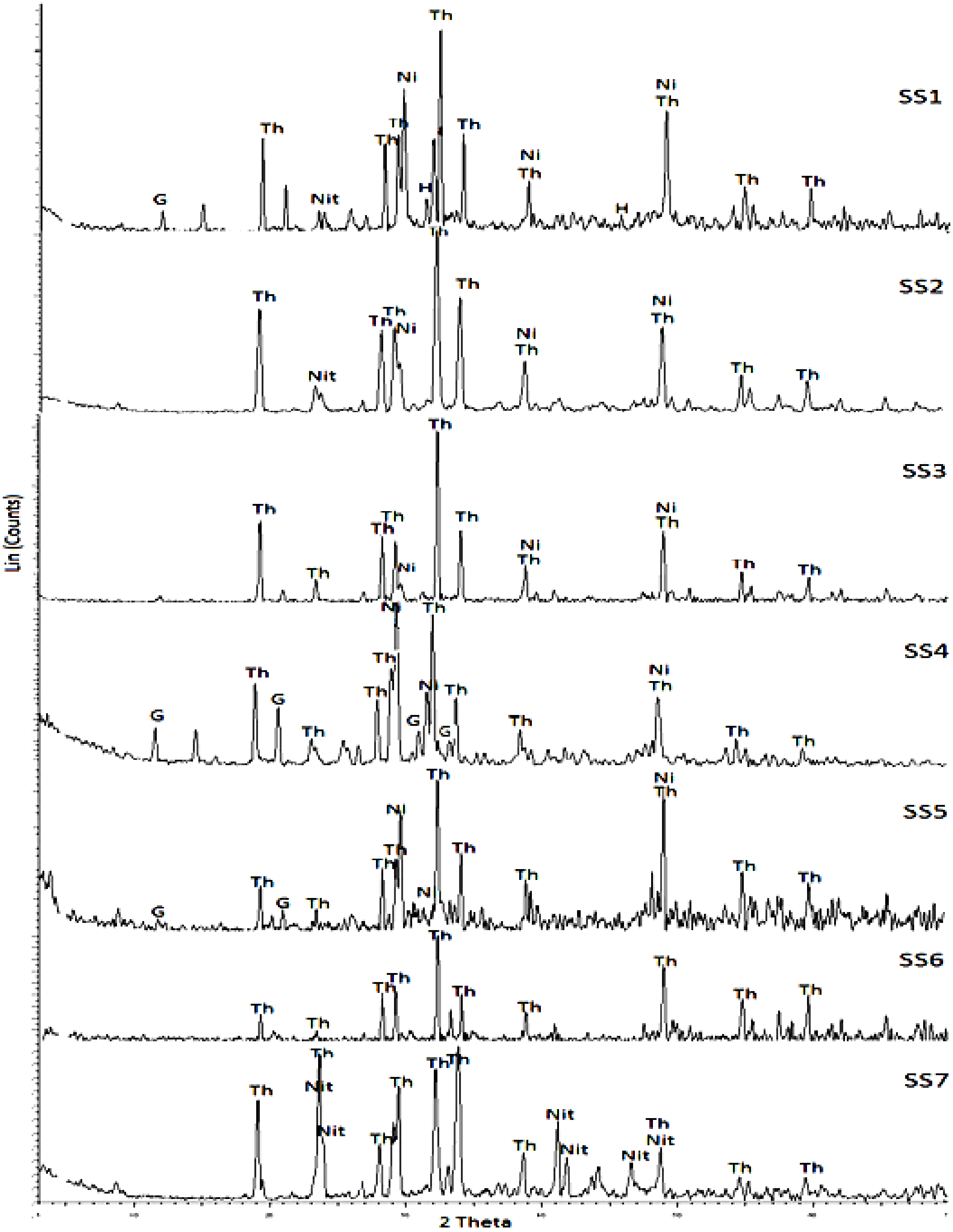


Figure 4.33 XRD traces of salt samples on the efflorescence zone of south eyvan façade, Sivas Gök Medrese

Th: Thenardite (Na_2SO_4), **H:** Halite (NaCl), **Na:** Natrite (Na_2CO_3), **Ni:** Nitratine ($NaNO_3$), **Nit:** Niter (KNO_3), **G:** Gypsum ($CaSO_4.2H_2O$), **Sy:** Sylvite (KCl)

XRD traces of salt samples prove the presence of salt crystals containing thenardite, nitratine, niter and gypsum on the walls having efflorescence problems.

Salt contents of the deteriorated original building materials were also examined. The tile mortar sample (STM) in powdered form was analysed qualitatively and quantitatively. It was the deteriorated part of the mortar. According to the conductometric studies, it contained 10% salt. After the conductımetric study, the salty water was recrystallized in laboratory conditions by drying and XRD patterns were obtained (Figure 4.34).

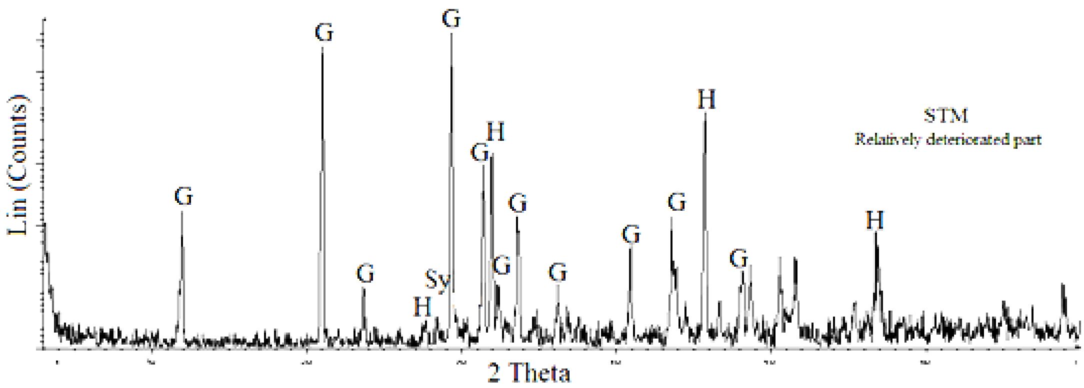


Figure 4.34 Relatively deteriorated part of STM was evaluated by extracting and recrystallizing its salty water. **G:** Gypsum ($CaSO_4.2H_2O$), **Sy:** Sylvite (KCl), **H:** Halite (NaCl)

Powdered brick samples were the most visibly deteriorated sample on the structure. XRD results proved the existence of salts in the brick samples. The salt percentage of the powdered brick samples were 7.8 % (SBr2) for Sivas Gök Medrese and 5.4 % (TBr2) Tokat Gök Medrese. Moreover, the XRD results showed that gypsum was the main salt in those bricks.

Figure 4.35 demonstrated the XRD results of Sivas Gök Medrese brick samples which were collected in different years. The first and second XRD traces of brick samples were taken in 1973 (SBr1) and 2010 (SBr2). Quartz, calcite and feldspar were the main minerals. After washing the sample, it was detected that only gypsum peaks were lost.

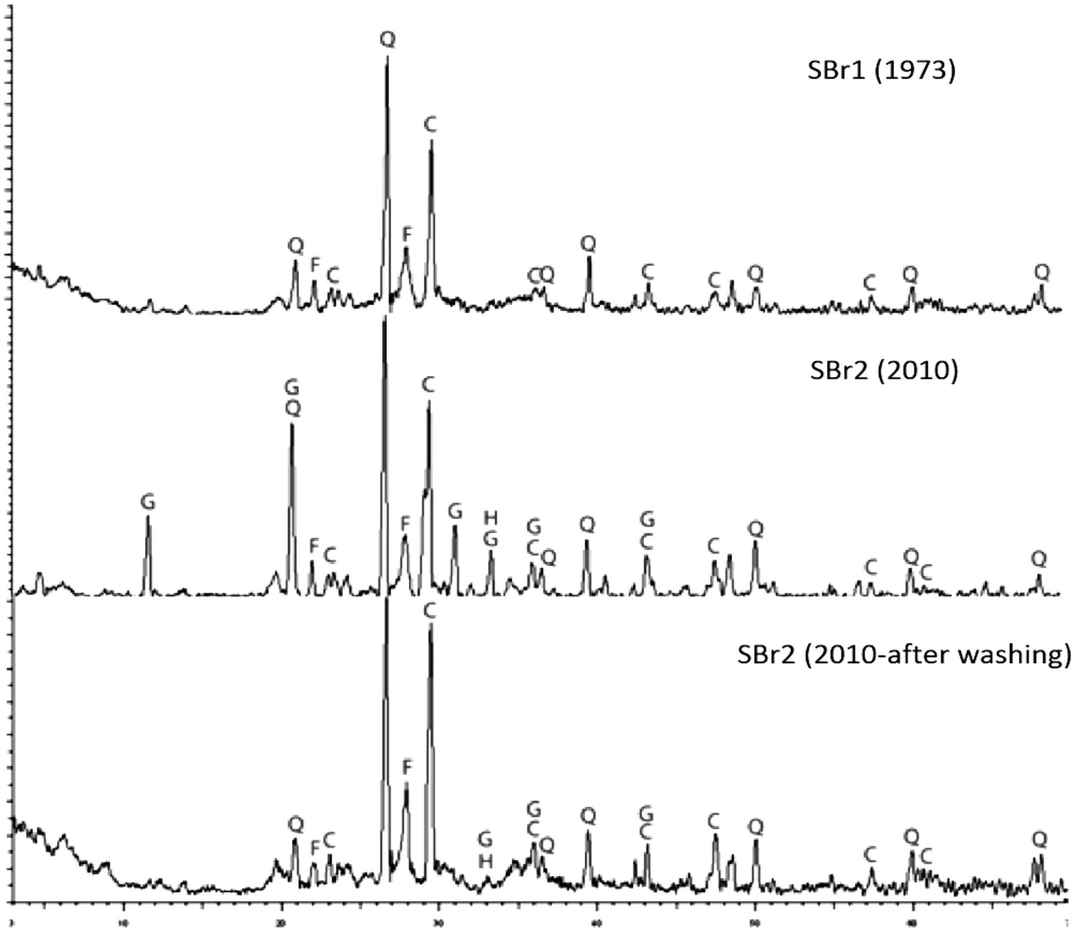


Figure 4.35 Original bricks of Sivas Gök Medrese showing gypsum as a salt before and after washing G: Gypsum, Q: Quartz, F: Feldspar, C: Calcite

Table 4.9 Results of spot test and XRD of south eyvan wall of Sivas Gökmedrese salt samples from the efflorescence zone and from the building materials

Sample Codes	**Place in South Wall**	**Height on wall and place**	**Type of Anion (Spot tests)**	**Type of Salts (XRD)**
SS1	1. wall of South Eyvan	205-220 cm	SO_4^{-2}, NO_3^{-},CO_3^{-2}, Cl^{-}	Th, Ni, Nit, G, H
SS2		190-210 cm	SO_4^{-2}, NO_3^{-},CO_3^{-2}	Th, Ni, Nit
SS3		180-200 cm	SO_4^{-2}, NO_3^{-},CO_3^{-2}	Th, Ni
SS4		145-155 cm	SO_4^{-2}, NO_3^{-},CO_3^{-2}	Th, Ni, G
SS5		125-140 cm	SO_4^{-2}, NO_3^{-},CO_3^{-2}	Th, Ni, G

Table 4.9 (Continued)

SS6		110-125 cm	SO_4^{-2}, NO_3^-,CO_3^{-2}	Th
SS7		180-200 cm	SO_4^{-2}, NO_3^-,CO_3^{-2}	Th, Nit
SS8		150-200 cm	NO_3^-,CO_3^{-2} ,Cl^-	Th, Nit
SRM1		Window frame	SO_4^{-2}, NO_2^-, NO_3^-, CO_3^{-2} Cl^-	
SRM2		Window frame	SO_4^{-2}, NO_2^-, NO_3^-, Cl^-	
SBr2		Window frame	NO_2^-, NO_3^-, CO_3^{-2}, Cl^-	H, Na, Ni
STM		Laboratory Archive	NO_3^-,CO_3^{-2} ,Cl^-	Sy, Ni, Na

Th: Thenardite (Na_2SO_4), **H:** Halite (NaCl), **Na:** Natrite (Na_2CO_3), **Ni:** Nitratine ($NaNO_3$), **Nit:** Niter (KNO_3), **G:** Gypsum ($CaSO_4.2H_2O$), **Sy:** Sylvite (KCl)
(The same abbreviations were used in XRD analyses in Figure 4.33).

Figure 4.36 demonstrated the XRD results of Tokat Gök Medrese powdered brick samples which were highly deteriorated. XRD traces of brick sample from 2010 (TBr2) showed quartz, calcite and feldspar as main minerals and some gypsum. After washing the sample, gypsum peak almost disappeared, its peak was very weak.

A detailed qualitative analysis was done to detect salts rather than gypsum. The salts from powdered TBr2 was extracted and recrystallized by drying in the drying-oven, the remaining crystals were analysed with XRD.

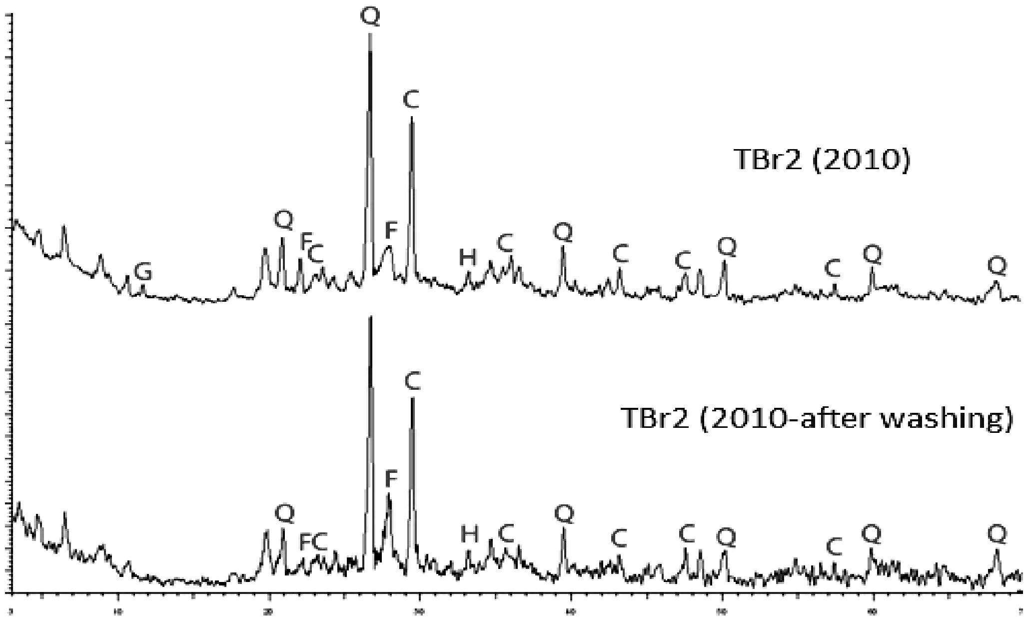


Figure 4.36 Original bricks of Tokat Gök Medrese showing gypsum as salt before and after washing G: Gypsum, Q: Quartz, F: Feldspar, C: Calcite, H: Hematite

It was seen that the highly deteriorated and powdered TBr2 contained halite (NaCl), sylvite (KCl) and gypsum ($CaSO_4.2H_2O$). Bassanite ($CaSO_4.1/2H_2O$) probably formed from gypsum after heating the sample for recrystallization at 40°C in the drying-oven for a night (Figure 4.37).

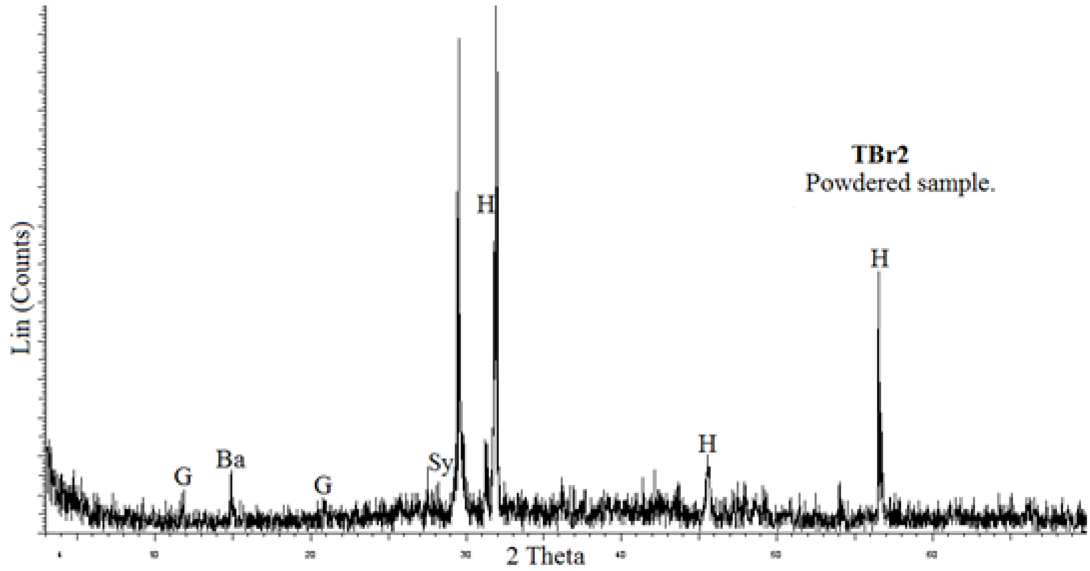


Figure 4.37 The XRD trace of salt residue of powdered brick sample (TBr2 of Tokat Gök Medrese). It was recrystallized in the drying-oven. G: Gypsum ($CaSO_4.2H_2O$), Sy: Sylvite (KCl), H: Halite (NaCl), Ba: Bassanite ($CaSO_4.1/2H_2O$)

Mortars, tile body and relatively healthy brick of Tokat Gök Medrese were examined by extraction and recrystallization of its salty water after the conductometric analyses. Some of them were dried by heating which caused the formation of bassanite from gypsum. Thus, TBr1 had gypsum, bassanite and nitratine ($NaNO_3$). TB7 had only gypsum, TM2 had gypsum, bassanite and nitratine, TM3 had gypsum and niter and TM5 had gypsum, bassanite, niter (KNO_3) and halite (NaCl) in their contents (Figure 4.38).

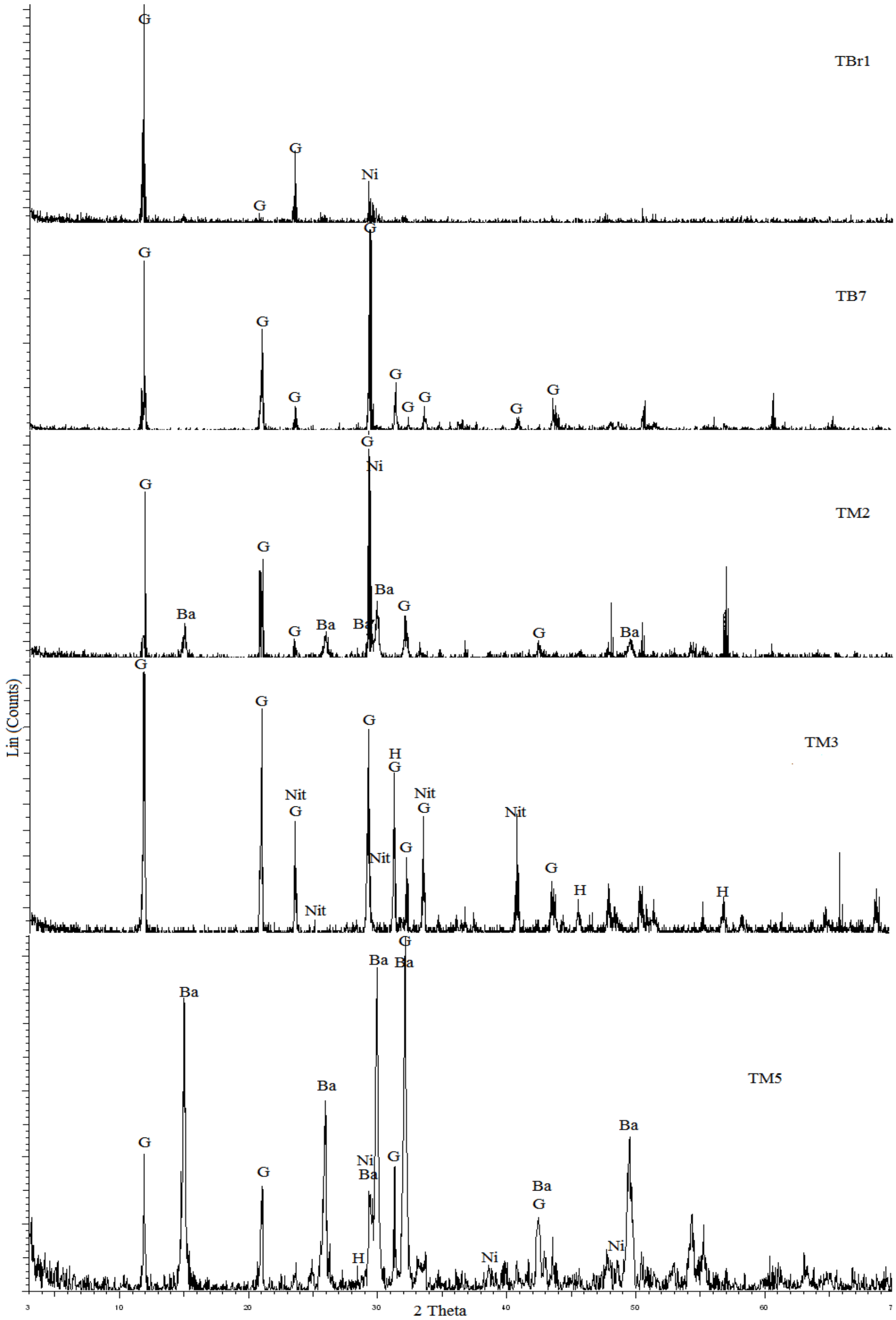


Figure 4.38 XRD of salt crystals after drying the salty solutions of Tokat Gök Medrese tile and mortar samples (G: Gypsum, Ba: Bassanite, Ni: Nitratine, Nit: Niter, H: Halite)

Table 4.10 Type of anions and salts in the mortar, brick and tile body samples of Tokat Gök Medrese

Sample Codes	**Place**	**Height on the wall**	**Type of Anion (Spot tests)**	**Type of Salts (XRD)**
TBr1	Left side of main eyvan facade	~105 cm	NO_3^-	Ni, G
TBr2		~95 cm	PO_4^{-2},SO_4^{-2}, Cl^-, NO_2^-, NO_3^-,CO_3^{-2}	H, Sy, G
TB7		~200 cm	PO_4^{-2}, SO_4^{-2}, CO_3^{-2}	G
TM1		~130 cm	PO_4^{-2}, SO_4^{-2}, Cl^-, NO_3^-	
TM2		~120-125 cm	PO_4^{-2}, SO_4^{-2}, Cl^-, NO_3^-	G, Ni
TM3		~100 cm	PO_4^{-2}, SO_4^{-2}, Cl^-, NO_3^-, CO_3^{-2}	G, Nit, H
TM4	Right side of main eyvan facade	~100 cm	SO_4^{-2}, Cl^-, NO_2^-, NO_3^-	
TM5		Taken from the ground	PO_4^{-2}, SO_4^{-2}, Cl^-, NO_3^-	G, Ni, H

H: Halite (NaCl), **Ni:** Nitratine ($NaNO_3$), **Nit:** Niter (KNO_3), **G:** Gypsum ($CaSO_4.2H_2O$), **Sy:** Sylvite (KCl)

4.5.2.3 Cross Section and SEM-EDX images of Salts

The presence of salt crystals were detected in cross sections and documented with stereomicroscope for Sivas Gök Medrese tile mortar (STM) (Figure 4.39).

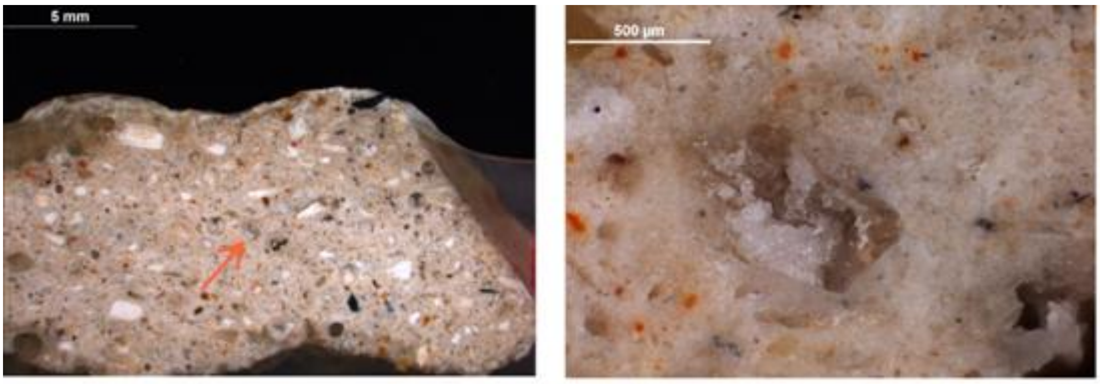


Figure 4.39 Sivas Gök Medrese tile mortar sample and their salt crystals in the pores which was shown with an arrow

In the Tokat Gök Medrese mortar (TM1) its salt crystals in the pores were documented by stereomicroscope (Figure 4.40).

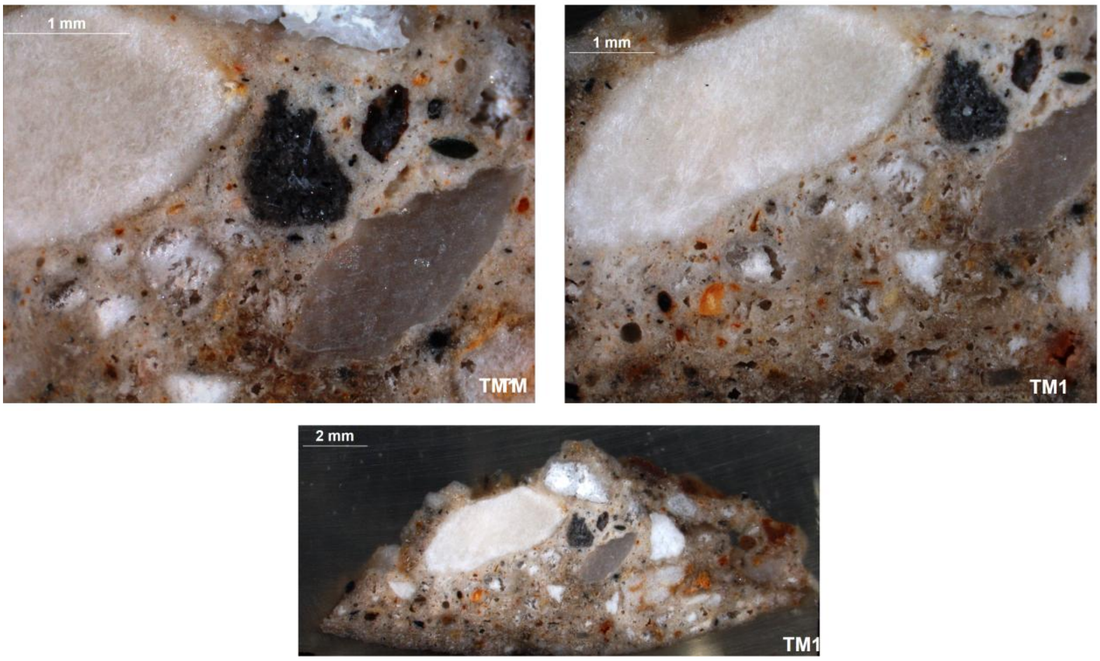


Figure 4.40 Tokat Gök Medrese mortar sample (TM1) and their salt crystals in the pores

The salt crystals were also detected with SEM. Figure 4.41 showed the surface of the Tokat Gök Medrese brick sample (TBr1). The salt accumulation was seen on the surface. The XRD results showed that they were gypsum crystals.

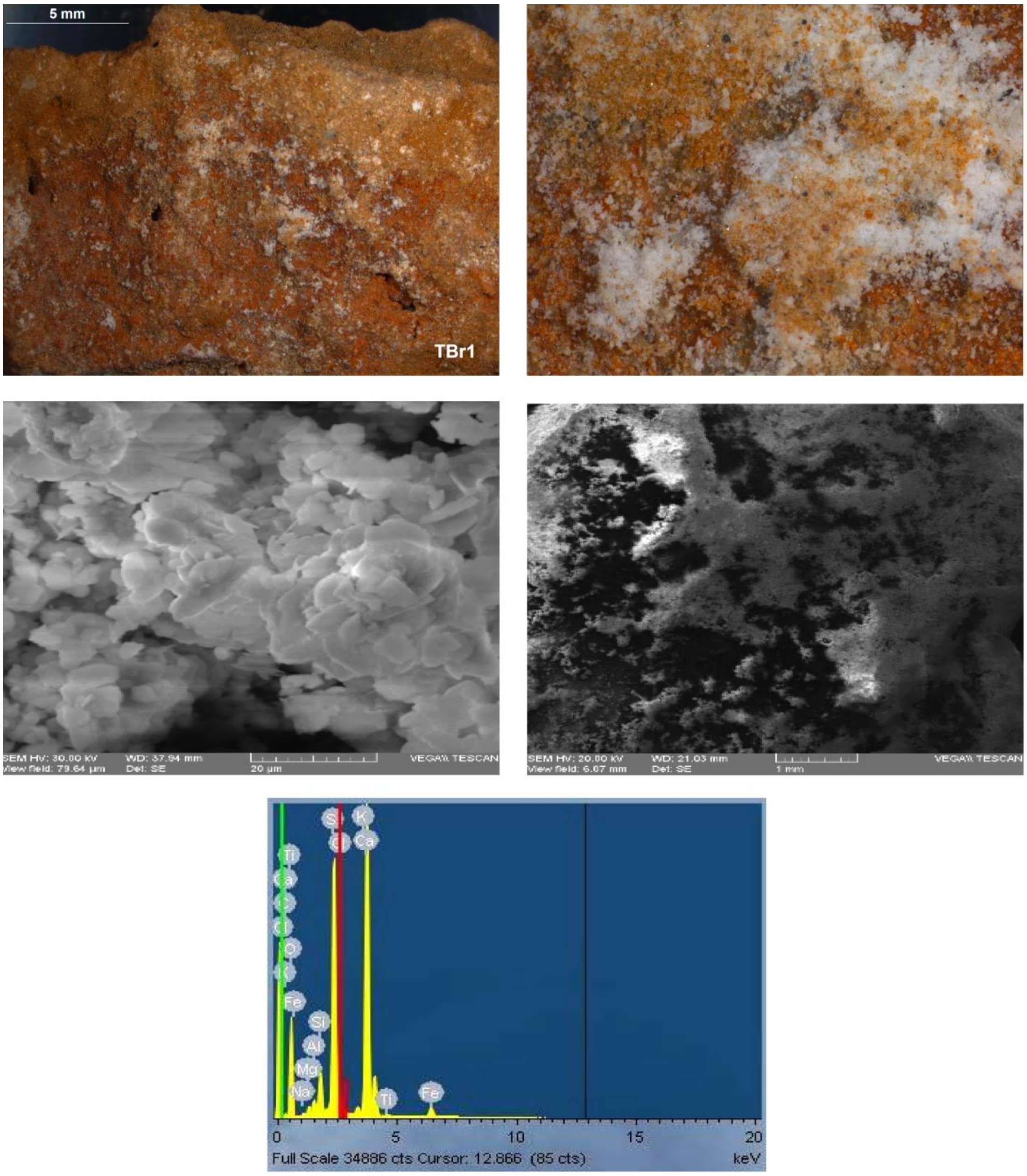


Figure 4.41 Tokat Gök Medrese brick sample (TBr1) and salt crystals on the surface.

4.6 Salts and Their Interaction with Relative Humidity Fluctuations of Environment

The relative humidity fluctuations cause crystallization-recrystallization cycles of the salts which increased their adverse effects on porous materials, depending on the equilibrium relative humidity of the specific salts.

In this study, the effects of R.H. fluctuations on the specific salts were examined. The equilibrium Relative Humidity (%) values of the salts were known from the literature at specific temperatures (Table 1.1). The equilibrium relative humidities of the salt mixtures were expected to be lower than their individual pure forms. The R.H. fluctuations of Tokat and Sivas were discussed in a section A. 7 and Figure 2.7.

As shown in Figure 4.42, the R.H. fluctuatins was between 40-50% and 90-100% in a specified day for Sivas. Also, the $R.H_{eq}$ of niter, nitratine, natrite, thenardite and halite were between those ranges. For that reason, all the salts were under cyclic crystallization-recrystallization in the monument.

According to Figure 4.43, the R.H. fluctuatins were between 60-70% and 90-100% in a specified day for Tokat. Also, the $R.H_{eq}$ of niter, nitratine and halite were between those ranges. For that reason, all the salts were under cyclic crystallization-recrystallization in the monument.

The column of gypsum was blue in the figures because it was accepted to be less affected from the R.H. changes.

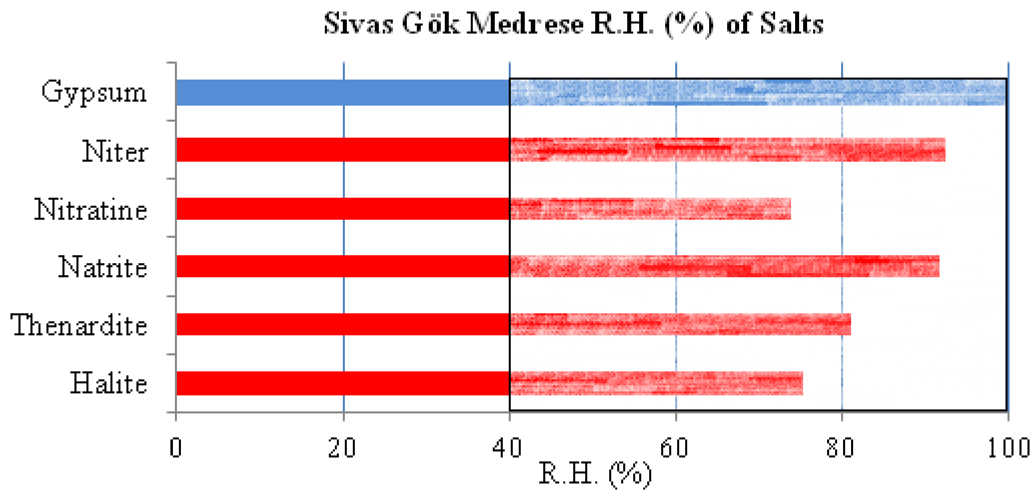


Figure 4.42 Equilibrium Relative Humidity ($R.H_{eq}$) of salts of Sivas Gök Medrese and its max. and min. R.H. changes in a day (August'11)

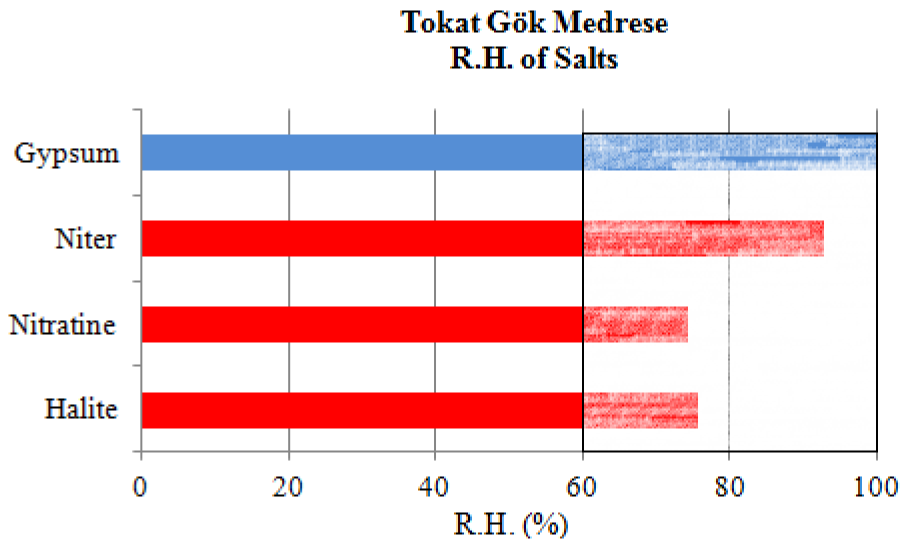


Figure 4.43 Equilibrium Relative Humidity ($R.H_{eq}$) of salts of Tokat Gök Medrese with its max. and min. R.H. changes in a day (August'11)

CHAPTER 5

DISCUSSION AND CONCLUSION

In this chapter, the results of the analyses were evaluated in terms of the technological features of the historic tiles and mortars, salt problems introduced to the structure by the recent repairs and other possible sources as well as suggestions for the particular salt extraction methods. The relation between the salt problems and the state of deterioration was investigated by the assessment of salt weathering in historic tiles and mortars and their progress. In this regard, the historic samples collected from the structures at different periods (1973, 1997 and 2010) were compared with each other in terms of the amount and type of soluble salts. Their damaging effects on the materials were discussed by comparing the climatic conditions of Sivas and Tokat. The discussion was done to decide the most effective method to extract salts from the monument. Within this context, future studies were suggested.

The study has started with visual analyses of decay forms. The visual documentation of decay forms were done on the non-rectified photograph of the Tokat Gök Medrese main eyvan façade to get approximate quantities of decay forms and their distribution. The decay types were mainly the material losses or the detachments.

According to the calculations, visibly healthy area was less than a half (Figure 4.1). The remaining part was visibly deteriorated. Main deterioration forms were loss and detachment of materials such as glaze, tile blocks, tiles and bricks. They were shown in Figure 4.2.

In the upper parts of the façade, the lost parts of tiles were filled and covered with repair plaster layer which was on the upper parts of the façade near the roof. Although the type of material damage under the plaster layer was not known, it was estimated that the tiles were exposed to rain fall and rain penetration due to faults in roof drainage system. Further, the tiles were open to direct effects of environmental conditions such as temperature, humidity changes and wind. Consequently, the upper side of façade had more wetting-drying and freezing-thawing cycles due to the climatic conditions of the region. While solar radiation helped drying out of the façade quickly, continuous water penetration from the roof resulted in the detachment and loss of tiles. In addition, in the upper zones between the repair plaster layer and tiles, it was also seen the loss of tiles from its mortar (7.6%). They were the evidence of continuing dampness problem.

In the lower parts of the wall, up to ~300cm from the ground, ‘crumbling and loss of bricks’, ‘detachment of tiles and tile blocks’, ‘loss of tile blocks’ and ‘partial loss of tile blocks’ were the main deterioration forms. The tiles neighbouring to the new repairs had suffered from severe salt weathering due to the high amount of nitrate, chloride and sulfate ions. In that region, rising dampness from the ground through the porous material carried salts from the ground. Also, the soluble salts from the inappropriate restoration materials dissolved and penetrated to the surrounding materials. For that reason, the materials at the lower zone were affected by the salt crystallization cycles. Salt could decrease the transportation of water; therefore, the drying rate decreased so that water remained longer in bricks (Franke, 1994).

In and around the same zone on the wall, only bricks behind the tiles were in powdered form while tile bodies had not the same deterioration types. According to the XRD results, the powdered brick sample (TBr2) had **halite** (NaCl), **sylvite** (KCl) and **gypsum** ($CaSO_4.2H_2O$). In the same region, the relatively sound brick sample (TBr1) had **nitratine** ($NaNO_3$) and **gypsum** in their salt contents. Although TBr2 had lower salt content (5.4%) than TBr1 (11.5%) the former was in powdered form in the masonry (Table 4.8). Those two bricks differed in the type and characteristics of their salts. TBr2 had two; TBr1 had one salt type except gypsum. Increasing the type of salts caused lowering the $R.H_{eq}$ (Arnold and Zehnder, 1989). Thus, lowering the $R.H_{eq}$ of the solution might cause more cyclic crystallization-recrystallization process which would result in more damage to the material. Gypsum had less effect on the crystallization process through the changes of ambient R.H. because it had higher $R.H_{eq}$ (99.6% at 20°C) than the others (Table 1.1). While gypsum was in contact with water from rain penetration or rising damp, it could partially dissolve and move through the porous media. That was why all brick and tile bodies had gypsum in their contents.

The XRD results of the powdered bricks proved that they contained calcite (Figure 4.35 and Figure 4.36). Presence of calcite might be due to several reasons. Calcite might be present in the raw material of the bricks or it might also be transported to bricks with water. The presence of calcite was examined in thin section analyses of Sivas Gök Medrese glazed brick sample (Figure 4.20). Calcite was present as micritic calcite crystals. Calcite was added to raw material of the glazed bricks, firing temperature of bricks must be below 800°C.

The L*a*b values of tile mortar, body and glazes were evaluated. Although the main minerals of tile bodies were similar (Figure 4.23), their firing temperature, preparation conditions and raw material properties might result in difference in color. For instance, the higher the firing temperature, more intense the colors of bricks are. Moreover, the oxidizing/reducing condition of the kiln was related with the intensity of red color which meant the change in the degree of oxidation of iron (Franke et al, 1998).

According to color measurements, the redness (+a) was higher in TB in comparison to SB but it was not validated by the EDX results of the tile bodies which was done by Özer et al, 2001.

The color measurement was also a clue for the original firing temperatures of the clay samples. It was expected that at least one variation in the values either a* or b* may be an indicator of different firing temperatures (Mirti and Davit, 2004). Although the color values were slightly different from each other, the firing temperature was estimated to be about 800°C for both of the medrese tiles (Özer et al, 2001).

Bulk density and effective porosity values of tile bodies and mortars were evaluated and compared with the repair mortars. It was shown that the historic tile and mortar samples had low bulk density and high porosity values. The bulk density of mortars was lower than tile bodies for both of the medreses, while the repair mortars of medreses were found to have higher bulk density and lower porosity than the historic tile and mortar samples.

The bulk density and porosity values of tile mortars and bodies were also compared with the other mortars of Seljuk Monuments (Tunçoku, 2001); while the properties of original ones were similar, the repair materials had higher bulk density (SRM2) and lower porosity (SRM1, SRM2) (Figure 4.4).

The repair mortars of Tokat Gök Medrese were applied on the lost parts of tile blocks. Their application date was not known. They had quite higher bulk density values and the porosities were lower than the original materials. For example, TM4 had considerably higher bulk density value (1.87 g/cm^3) (Table 4.3).

The tile mortars of Sivas Gök Medrese and Tokat Gök Medrese had quite the same bulk density and porosity values but their tile bodies were quite different. SB had higher density and lower porosity values than TB. In addition, the repair mortars of Tokat Gök Medrese had higher density and lower porosity values.

The **mechanical properties** of mortar and tile body samples were estimated by measuring modulus of elasticity values with ultrasonic pulse velocity and bulk density measurements. Moduli of elasticity of Sivas Gök Medrese mortar samples had the average value of 4.8±0.6 GPa. The tile bodies of Tokat Gök Medrese had the average 2.5 ±0.9 GPa (Table 4.4). The average modulus of elasticty values of 14 brick masonry mortars of Seljuk monuments were 1.6±0.7 GPa(Tunçoku, 2001). Those values indicated that the mortar and the tile bodies had sufficient mechanical properties.

Compositional Properties of Tiles and Mortars

The experiments on the **binder-aggregate ratios** of historic gypsum mortars showed that Sivas and Tokat tile mortars were mainly composed of gypsum. The remainings were calcite and aggregates for both of the tile mortars of the medreses. A detailed mineralogical study was needed for the calcite content of mortars. It might be added as a binder or aggregate such as limestone pieces to the mortar.

According to Middendorf and Knöfel (1998), it was estimated that the smaller amounts of aggregates in the gypsum-based mortars were the ‘impurities’ of the raw material, because they were too small to change the technological properties of mortar (Middendorf and Knöfel vd. 1998). The aggregates were analyzed in detail with XRD and stereomicroscope. The XRD results of the aggregates which were lower that 75µm showed that they were composed of mainly quartz, feldspar and hematite for both of the tile mortars of Sivas Gök Medrese and Tokat Gök Medrese. Also, the photographs taken in stereomicroscope showed that they contained some tile fragments with their glazes, quartz and ash particles in different dimensions (Table 4.6). Contrary of what was mentioned in the literature (Livingston et al, 1991), the aggregates seem to be used consciously for the production of tile mortars contributing to their technological properties.

The facades of the interior side of main eyvan had also cement-based application. Although they had no visible deterioration or water leakage at the moment, they must also be kept under observation because the investigated salts on the other facades could occur by the effect of R.H (%) fluctuations of the ambient air (Figure 4.43).

Sivas Gök Medrese had quite different problem because it was difficult to differentiate the original tiles from their imitations in most zones. The precautions against water leakage would not be enough to prevent salt damage since the salts determined, definitely would continue to give damage to the surfaces due to the fluctuations of R.H (%) in ambient air (Figure 4.42). The process of salt extraction by poultices should also be applicable for Sivas Gök Medrese eyvan tiles.

The pozzolanic activity measurements of brick and tile bodies were shown in Table 4.7. It was concluded that the pozzolanic activities of all the bricks and tile bodies were very high with respect to the classification of Luxan (1989). But it was surprising that the bricks (with an average conductivity value of ~21.3 mS/cm) were much more pozzolanic than the tile bodies (with an average conductivity value of ~2.3 mS/cm).

XRD traces of tile bodies show that the main mineral in their composition was quartz. A small amount of feldspar was present in both of the medrese tile bodies. Clay minerals were not found in the XRD traces. The traces of kaolin were lost at a temperature higher than 500ºC. The other clay minerals such as illite would be detected in XRD after heating if it was present. However, no traces of illite was determined in the composition of tile bodies, therefore kaolinite was thought to be the main clay mineral in the composition of tile bodies (Magetti, 1982).

Polished cross sections of tile bodies and mortars were examined to analyze the interaction of different parts of tile with its glaze and mortar. It was observed from the photos that the glaze combined well with the body of the tile. The thickness of the glaze was constant on the same sample. This meant that glaze powder was prepared and then applied on the body followed by the firing process in the furnace (Tite and Bimson, 1986).

The **image analysis** of cross section of Sivas Gök Medrese tile mortar was studied with Leica Application Suite software. The visibly bigger gypsum lumps were drawn to determine their total amount in the mixture (Figure 4.16). According to the manual calculations, gypsum lumps were about 7% of the total area. For more precise results, the number of studied samples and their surface area must be increased. XRD analysis was conducted to detect the composition of the lumps. No other peaks were detected other than gypsum in the XRD traces (Figure 4.28). In the study of image analysis, the total amount, distribution and dimension of pores could be detected with an optical microscope.

The Salts Detected

In this study, qualitative and quantitative analysis of soluble salts were investigated with several experiments. The analyses proved the existence and amount of salts in brick samples. In addition, the soluble salts from the efflorescence zone of Sivas Gök Medrese were examined with XRD.

Sivas Gök Medrese

Some salt contents were compared to detect the difference in years. While Sivas Gök Medrese tile body samples had the average of 1.1±0.7 % salt content in 1997, it increased to 7.8% for the brick sample in 2010 (SBr2).

The recent repair mortar samples of Sivas Gök Medrese had also high soluble salt contents. It was the average of 9.5% (SRM1 and SRM2). They could be evaluated as a salt source on the wall because there was an efflorescence zone on the repair mortars of the south eyvan wall of Sivas Gök Medrese. They were also examined with XRD (SS1, SS2, SS3, SS4, SS5, SS6, SS7 and SS8). The salt samples were mainly **thenardite** (Na_2SO_4), **nitratine** ($NaNO_3$)**, halite** (NaCl), **natrite** (Na_2CO_3), **niter** (KNO_3), **gypsum** ($CaSO_4.2H_2O$) and **sylvite** (KCl) which were taken in different heights of the wall.

XRD results of the salts were also supported by the existence of NO_3^-, SO_4^{-2}, Cl^- and CO_3^{-2} ions in spot tests.

According to Arnold and Zehnder (1989), the alkaline salts were the result of the use of Portland cement which supplied alkaline ions and converted alkaline earth sulfate, nitrate and chloride salts to alkaline salts. They were more harmful because of their higher crystallization abilities in a humid atmosphere. In this study, all the detected salts were the alkaline which were the evidence of using Portland cement (Arnold, 1981). During restorations, ‘Polyfilla Interior’ was mentioned in the reports that were applied on the lost parts of tiles with hydraulic lime mortar during the restoration of Sivas Gök Medrese. It was high strength cement with low porosity. That could cause local dampness problems as well as salt contamination.

In Figure 4.36 the original sample was in powder form (SBr2). It was taken in the area with rising damp problem. XRD analysis was performed before and after washing the sample. Gypsum disappeared after washing the sample in XRD traces since gypsum had low solubility that its damage process was slow which formed within a few years to many years (Arnold, 1998). In present condition, the brick was in contact with the gypsum based tile mortar, so the source of gypsum was mostly the original tile mortar. The dampness problem and microclimatic changes in the monument caused the gypsum to be transported to brick having higher porosity (porosity of SB; 39±1 %; Figure 4.4).

Tokat Gök Medrese

The increasing proportion of salt was also detected in Tokat Gök Medrese tile and brick samples. While the tile bodies had average of 3.4±0.9% salt content in 1997, the amount increased to 10.1 % for TB7 in 2010. It was clearly seen that there were higher salt contents in the samples which were collected in 2010.

All the mortar samples of Tokat Gök Medrese had Cl^-, NO_3^- ions. They also had PO_4^{-2} ion except TM4. CO_3^{-2} ion was only present in TM3. The experiments were also performed with original and restoration materials such as bricks and repair mortars. They were also shown in the table (Table 4.10).

Powdered brick samples were in the worst condition. XRD results proved the existence of salt minerals, which were the main cause of deterioration. The salt percentage of the powdered brick samples was 5.4% for TBr2. Moreover, the XRD results show that gypsum, halite and sylvite were the main salts in those bricks which was similar to the powdered brick samples of Sivas Gök Medrese. XRD results indicated that the brick was in contact with the gypsum based mortars. Powdered brick samples were taken from the surfaces where tiles were lost. Therefore the mortars were more in contact with the atmospheric conditions as rain water and air pollution. The distribution of salts among the interior sides must also the examined.

Another potential danger was the formation of ettringite ($3CaO.Al_2O_3.3CaSO_4.31H_2O$). Therefore, the monuments must be protected from dampness and Portland cement applications that were potential danger for both of the medreses (Böke et al, 2003).

Moreover, Franke (1994) stated that salt containing bricks had decreased vapor diffusion transport. Thus, it caused a decrease in the drying rate of brick, and brick was more susceptible to the frost action related with the climatic conditions. Also, the hygroscopic properties of salts caused the bricks to be exposed more to the humidity problems and damage by frost action (Franke et al, 1998).

For the deactivation of salts due to relative humidity changes and condensation processes, the climatic conditions of the environment must also be taken into account (Arnold, 1998).

The **pore size distribution** of tile body and mortar samples was investigated by Mercury Intrusion Porosimetry and shown in graphs (Figure 4.8, Figure 4.9, Figure 4.10, Figure 4.11, Figure 4.12). The individual pore size distributions showed that the tile bodies and glazed bricks (TT and SGB) had higher pore sizes with respect to tile mortars (TTM and STM), which were adjacent to tiles. As it was known, the salt solution prefered to penetrate into pores with lower pore dimensions. The conductivity results proved the idea that the salt contents of tile mortars were higher than tile bodies (Table 4.8). Another reason of higher salt contents of mortars might be that the mortars had the interaction with air where drying occurred while the tiles had glazes to prevent the interaction of tiles with air. As a result, the salty solution might penetrate into tile mortars more than the tile bodies.

The pore sizes of Tokat Gök Medrese tile body sample (TT) and its tile mortar (TTM) were in a wide range being 0.008μm and 211.1μm. That range was narrower for the tile and mortar samples of Sivas Gök Medrese when compared to the samples of TGM. Their pore size distribution was between 0.021 μm to 73.2 μm. Pore size distributions of the poultices must be smaller than 0.008μm for Tokat Gök Medrese and 0.021 μm for Sivas Gök Medreses. The smallest pore sizes were not so different for the samples of both medreses. The most suitable poultices for salt extraction must be developed considering the pore size distributions of the tile and mortar samples. Those poultices must be proper for the tiles and mortars because they were in touch with each other on the masonry. Recent studies on the preparation of suitable poultices showed that some kaolin-sand mixtures with the proportion of 1:3 by mass had the smallest pore size distribution (Figure 1.8). Such a poultice had pore diameter peaks at 0.3 μm and 5μm. It was a dry poultice prepared by standard kaolin and sand fragments with 0.08–0.5μm. The water content of that poultice expressed as weight water/weight dry poultice ratio was at 0.22 (Lubelli et al, 2010).

The efficiency and workability of the possible poultices must be investigated in the laboratory then in-situ studies must be organized on the monument. In theory, kaolin-sand based poultices were more suitable as mentioned above.

Poultice application for a façade with tiles should be a quite different process than stone or brick surfaces because of the glazed surfaces of tiles. Tokat Gök Medrese and Sivas Gök Medrese had inappropriate repairs either on the surface or at the masonry. The cement-based repairs and the water leakages were causing efflorescence problem for the tiles and masonry. For that reason, before application of the poultices, all the possible salt and water sources must be eliminated from the masonry. After the removal of the repair mortars, the remaining original material must be investigated to determine the type and depth of the salts as well as the efficiency of the poultices.

Tiles, gypsum-based tile mortars, bricks and their mortars were together in the masonry. Thus, the properties of the poultice must be suitable for all those materials. One contradiction was the movement of the salty solution. It might move from the tiles having bigger pores to the mortars or to the poultice having smaller pores. Success could be achieved by repeated poultice application to the surface. Another contradiction was gypsum which was slightly soluble raw material of the tile mortars. Even if some additives might be added to reduce the solubility of gypsum, it could behave as a salt in liquid environment. Some studies showed that the efficiency of the poultices were not effective or low for SO_4^{2-} ions (Bourgés et al, 2008). The other disadvantage was the aesthetics. Kaolin-based poultices had white deposit on the surface after the removal of the poultice. For our case it might be better to apply the poultices on the lost parts of glazed tiles, not on the surface of the glazed tiles. Some solutions had to be found for prevention of white deposit formation due to application of poultices. The treated zones must be monitored for the possible side effects.

The process might be more suitable with Tokat Gök Medrese main eyvan façade because the original tiles and the new plasters were observed. As seen in Figure 4.2, 55.1% of the façade had different deterioration forms such as crumbling and loss of materials.

Conclusion

In this part, the experiments on tiles, their mortars and bricks from Tokat Gök Medrese and Sivas Gök Medrese were evaluated to explain their technological properties and deterioration problems in order to propose some conservation treatments.

The examination of the tiles, tile mortars, bricks and their mortars of Sivas Gök Medrese and Tokat Gök Medrese revealed their technological characteristics and deterioration by salt weathering.

Documentation of visual decay forms of Tokat Gök Medrese tiles and mortars were done with AutoCAD on the photograph of the facade. Relative area of each deterioration form was calculated. Loss of tiles was the main decay form among the others. The deterioration forms were more abundant over the upper and lower sides which were near to the dampness zones from the roof and above the ground.

The bulk density and porosities of tile body and mortar samples were determined while the original ones were similar; the repair mortars had higher bulk density and lower porosity in both of the medreses. Modulus of elasticity of tile body and mortar samples were determined and compared with the other Seljuk building materials. Mortar and the tile bodies had sufficient mechanical properties as indicated by their E_{mod} values.

The pore size distributions of tile and mortar samples were examined. It was shown that the tile bodies and glazed bricks (TT and SGB) had higher pore size values with respect to tile mortars.

Mineralogical compositions of the tile body, glazed bricks and tile mortars of Sivas Gökmedrese and Tokat Gökmedrese were analyzed with XRD and thin sections. The tile bodies had coarse quartz crystals as temper, feldspar, plagioclase minerals, clays as limonitized opaque minerals and metamorphic rock fragments. The glazes had quartz, feldspar and cassiterite on their XRD traces. The glazed bricks had angular and sub-angular shapes of large grains as temper which was polycrystalline quartz. In addition, hematite, plagioclase feldspars and biotite was present. Calcite was present in the matrix. The tile mortars had gypsum, micritic calcite lumps, quartz and charcoal or coal fragments.

The pozzolanic activities of all the bricks and tile bodies were extremely high with respect to the classification of Luxan et al (1989).

Qualitative and quantitative analysis of soluble salts were investigated with several experiments. The deteriorated samples and salts on the efflorescence zone were examined to determine the types of salts in the original materials. Spot tests were done to detect the salt ions of materials. In addition, the salt crystals were identified with XRD.

The analyses proved the existence and amount of salts in brick samples. The alkaline salts were the result of the use of Portland cement which supplied alkaline ions and converted alkaline earth sulfate, nitrate and chloride salts to alkaline salts. They were more harmful ones because of their higher crystallization abilities in a humid atmosphere since all the detected salts were the alkaline salts that were the evidence of Portland cement damage in the two monuments.

The relative humidity fluctuation of the environment was compared with that of salt characteristics. It was seen that the tiles were adversely affected from salt crystallization.

The best desalination methods were discussed for the salts. Advection based methods were suggested. The most important property of the poultices must be their smaller pore size distribution than original salty materials. The pore size distribution of the original materials were analysed and compared to determine the best type of poultice from the literature. It was concluded that kaolin-sand mixtures (0.08mm-0.5mm) in a proportion of 1:3 by mass and 0.22 (weight water/weight dry poultice) was the best one when the pore size distribution of the tiles and mortars were considered. The study on material properties and desalination process was expected to help maintenance of monuments having salt problem.

Tiles, gypsum-based tile mortars, bricks and their mortars were together in the masonry. Thus, the properties of the poultice must be suitable for all those materials.

Desalination by advection might be more suitable with Tokat Gök Medrese main eyvan façade because the original tiles and the repair with new plasters were observable. 55.1% of the façade had different deterioration forms such as crumbling and loss of materials and new plaster application (Figure 4.2). In Sivas Gök Medrese it was difficult to detect the original tiles from the imitation tiles in most of the zones.

Future Studies

Some further studies were needed for more accurate results such as detection of salt minerals in the pores with SEM-EDX to better understand the salt damage mechanism and develop desalination methods.

Further studies are necessary to measure the capillary suction properties and water vapor permeabilities of the tiles and their bodies to understand the movement of salty water through those materials.

Additional works are needed to detect the durability characteristics of original gypsum mortars and their inorganic and organic additives because it was seen that the broken tiles were attached to walls with incompatible repair mortars (Tokat Gök Medrese- November 2010). It is necessary to develop proper repair mortars for future conservation studies.

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