CHARACTERIZATION OF HORASAN PLASTERS FROM SOME OTTOMAN BATHS IN İZMİR

A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

in Architectural Restoration

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July 2005
İZMİR

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ACKNOWLEDGEMENTS

I gratefully acknowledge to my supervisor Assoc. Prof. Dr. Hasan Böke for the scientific guidance and valuable contributions he has provided throughout the study. Without his kind support, remarkable patience and critiques this thesis might not have existed.

I am much indebted to Assoc. Prof. Dr. Başak İpekoğlu who have contributed much to my education, for her helps and support, and for sharing her knowledge whenever I need.

I am grateful to Assist. Prof. Dr. Selim Sarp Tunçoku for his kindness and morale support during this study.

I am also thankful to the jury members Assoc. Prof. Dr. Murat Günaydın and Assist. Prof. Dr. Selim Sarp Tunçoku for attending my thesis jury and for their valuble contributions.

I would like to thank Res. Assist. Özlem Çizer for her support and helps during the experimental studies; and Res. Assist. Kader Reyhan for his helps during the sampling. I would also like to thank Res. Assist. Meral Budak for her patient helps in preparing the samples for laboratory analyses.

My thanks are also for the research scientists of the Centre for the Materials Research of the Institute for SEM-EDS, XRD and AFM analyses.

I am grateful to my dear friends Işıl Talu, Kerem Şerifaki, Özlem Aslan Özkaya and Sevinç Eğercioğlu with whom I survived really hard works together during our master education. To work with them was a great pleasure for me.

I owe my special thanks to Bengü Sevil for being the best of friends; Gencer Aydın for his helps and concern; and to Sercem Murat Sağın for his great patience and encouragement during this study.

Finally, I am forever indebted to my dear mother Rukiye Uğurlu and my dear father Hasan Uğurlu for the endless understanding, support and love they have never ceased to give me throughout my life. This thesis is dedicated to them.

ABSTRACT

Mortars and plasters of many Roman, Byzantine, Seljuk and Ottoman period buildings were produced by using lime as binder and crushed bricks or tiles as aggregates. These mortars and plasters are called as "horasan" mortars and plasters in Turkey. Horasan mortars and plasters have been widely used as waterproof materials in aqueducts, bridges, cisterns and baths due to their hydraulic properties and high mechanical strengths.

In this study, characteristics of horasan plasters used in some Ottoman bath buildings in Urla and Seferihisar in İzmir were investigated by using XRD, SEM-EDX, AFM and chemical analyses.

Physical, chemical and microstructural properties of plasters do not differ according to spaces, levels and layers generally. All of the plasters are porous and low dense. Multi layered horasan plaster application with the less porous finishing layers provide a waterproof surface to lower levels. Lime/aggregate ratios of horasan plasters are in the range of 1/2 and 3/2. Horasan plasters are hydraulic owing to the presence of pozzolanic brick aggregates. Crushed and powdered brick aggregates are good pozzolans since they were produced from raw materials containing high amounts of clay and they were fired at low temperatures.

On the other hand, bricks used in the domes of the baths were manufactured by using raw materials containing fewer amounts of clay minerals than those of aggregates. Due to the less amounts of clays in their compositions, they are not pozzolanic although fired at low temperatures. This result revealed that crushed brick aggregates were manufactured intentionally to use in horasan plasters.

Key Words: Ottoman Bath, Horasan Plaster, Brick, Lime, Pozzolan

ÖZET

Roma, Bizans, Selçuklu ve Osmanlı döneminde inşa edilmiş birçok tarihi yapının harç ve sıvalarının bazıları, bağlayıcı olarak kireç ve agrega olarak tuğla, kiremit gibi pişirilmiş seramik malzemeler kullanılarak hazırlanmıştır. Bu harç ve sıvalar ülkemizde "horasan" harç ve sıvaları olarak adlandırılmaktadır. Horasan harçları ve sıvaları, su altında da sertleştikleri ve yüksek dayanıma sahip oldukları için su kemerleri, köprüler, sarnıçlar ve hamamlar gibi su etkisi altındaki yapılarda kullanılmışlardır.

Bu çalışmada, Urla ve Seferihisar'da bulunan bazı Osmanlı dönemi hamam yapılarında kullanılan horasan sıvaların özellikleri XRD, SEM-EDX, AFM ve kimyasal analizler ile incelenmiştir.

Horasan sıvaların fiziksel, kimyasal ve mikroyapısal özellikleri kullanıldıkları mekana, seviyeye ve katmana göre büyük farklılıklar göstermemektedir. Sıvalar çok gözenekli ve düşük yoğunlukludur. Alt seviyede çok tabakalı horasan sıva kullanımı ve az gözenekli bitirme tabakası ile su geçirmezlik özelliği sağlanmaktadır. Horasan sıvalarında kireç/tuğla kırığı oranı ağırlıkça 1/2 ve 3/2 arasında değişmektedir. Horasan sıvaların hidrolik özellik taşıdığı, bu özelliğin ise tuğla kırıklarının puzolanik özelliğinden kaynaklandığı tespit edilmiştir. Tuğla kırıklarının puzolanik özellikleri, üretimlerinde kullanılan hammaddelerin yüksek miktarda kil içermesinden ve düşük sıcaklıklarda pişirilmelerinden kaynaklanmaktadır.

Hamamların kubbelerinde kullanılan tuğlalar, tuğla agregalardan daha düşük miktarda kil içeren hammaddeler kullanılarak üretilmiştir. Bu tuğlalar, düşük sıcaklıklarda pişirilmiş olmalarına rağmen, yapılarında az miktarda kil bulundurdukları için puzolanik özellik taşımamaktadır. Bu sonuç, horasan sıva yapımında kullanılan tuğlaların sıva yapımında kullanılmak üzere özel olarak üretildiklerini göstermektedir.

Anahtar Sözcükler : Osmanlı Hamamı, Horasan Sıva, Kireç, Tuğla, Puzolan

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CHAPTER 1

INTRODUCTION

1.1. Subject and Aim

Historic buildings are not only single works of architecture but also living witnesses and documents of ancient traditions, technologies, developments, craftsmanships, materials etc. Conservation studies of historic buildings must be done by safeguarding them for future generations[1].

The aim of the conservation studies in historic buildings must be to preserve the architectural, aesthetic and historic values of the building and must be based on respect for original materials and authenticity[1].

Conservation of historical buildings must recourse to all sciences and make use of all the knowledge, skills and disciplines which can contribute to study[2]. Specialists from different disciplines such as architects, civil engineers, chemists, art historians and archaeologists must collaborate for safeguarding of the architectural heritage. Only by this way, a full understanding can be provided not only for the architectural, aesthetic or historic characteristics of the building but also for the structural and material characteristics.

The characteristics of new materials used in restoration works and their compatibility with existing ones should be fully established[3]. This must include long-term effects of the new material in order to avoid further deteriorations. Thus, selection of compatible materials requires a detailed knowledge on characteristics of original building materials.

Brick-lime mortars and plasters are one of the most common and important materials used in construction of various historic monuments. Crushed bricks or tiles which were used as aggregates in lime mortars and plasters are known as "Horasan" in

[1] The Venice Charter, http://www.international.icomos.org/charters/venice_e.htm
[2] The Burra Charter, http://www.icomos.org/australia/burra.html
[3] ICOMOS Charter – Principles for the Analysis, Conservation and Structural Restoration of Architectural Heritage (2003), http://www.international.icomos.org/charters/structures_e.htm.

Turkey (Akman et. al. 1986), “Surkhi” in India (Spence 1974), “Homra” in Arabic Countries (Lea 1940) and “Cocciopesto” in Roman (Massazza and Pezzuoli 1981).

Horasan plasters are produced by mixing lime with crushed or powdered ceramic materials like bricks and tiles. Owing to the pozzolanic properties of crushed brick aggregates, horasan plasters have hydraulic characteristic and they set under water. Although the high humid and hot environment of bath buildings most of the original horasan plasters still exist because of their good durability and hydraulic properties. These characteristics can explain the common use of horasan plasters in bath buildings.

In historic bath buildings, conservation studies must be carried out by using new intervention plasters compatible with original horasan plasters. This requires a detailed knowledge on physical, mineralogical, chemical and hydraulic properties of horasan plasters.

There are lots of studies on characterization of brick-lime mortars and plasters. These studies were intended for determining basic physical properties, raw material compositions, mineralogical and microstructural properties of brick-lime mortars and plasters or for preparation of new brick-lime mortars for the purpose of conservation.

However, any information is not given about the differences or similarities of horasan plasters used in bath buildings, in different spaces of bath buildings and on different levels of the spaces in these studies.

The aim of this study is to investigate the characteristics of horasan plasters collected from different spaces, different levels and different layers of three relevant coeval bath buildings. It also aims to provide basic information about the properties that new horasan plasters shall have for the purpose of conservation.

1.2. Limits of the Study

Investigated horasan plasters were collected from bath buildings which is one of the building types horasan plasters had been used widely. Study is limited with Hersekzade, Kamanlı and Düzce Baths which were Ottoman Baths dated back to the 15th and 16th centuries (Reyhan 2004) located in Urla and Seferihisar. These buildings were selected since they were located very close to each other, constructed nearly in the same period, and they had similar construction techniques. Furthermore, these buildings are very important because they have survived until these days preserving their original material characteristics. However, within the passed hundreds of years, any conservation study had not been performed; and these bath buildings which can be considered as historic documents of local craftsmanship, architectural and cultural values are now under threat of extinction. Only, their construction techniques (Reyhan 2004) and lime mortar characteristics (Çizer 2004) have been determined for the purpose of conservation.

Plasters played an important role in surviving of these baths in spite of high temperature and humid environment conditions. However, any investigations on horasan plasters whether they had been produced intentionally for bath buildings or not have not been done until now. Although this study is limited with three bath buildings, results achieved from this study will guide to further researches which will be carried on plaster technologies of other bath buildings.

1.3. Method of the Study

Method of the study includes sampling and experimental studies. Sampling was carried out by collecting plaster samples from soyunmalık, ılıklık, sıcaklık and halvet spaces of baths considering plaster application techniques as levels and layers of plasters, and by collecting building bricks from domes of the baths. Experimental studies were carried out in order to determine physical properties and raw material compositions of plasters; pozzolanic activities of crushed brick aggregates and building bricks; mineralogical and chemical compositions and microstructural properties of plasters, crushed brick aggregates and building bricks; and hydraulicity of plasters. Results of these studies were given and discussed among themselves and with other results achieved in recent studies.

Within this context, functions of plasters in buildings, characteristics of raw materials used in mortars and plasters of historic buildings and general information about horasan plasters are given in the second chapter. In the third chapter, plaster characteristics according to the spaces of the baths, sampling of plasters and building bricks, and method of experimental studies are described. In the fourth chapter, results of the experimental studies are evaluated and discussed. Finally, the conclusions of the study are given in the fifth chapter.

CHAPTER 2

PLASTERS

2.1. Properties and Functions of Plasters in Buildings

Plasters and renders are secondary non-structural components of a building applied on primary structural system elements in order to provide protection against external agents as well as an aesthetic appearance, a smooth, continuous surface for painting or decoration, and hygiene (Matero 1995, Holmes and Wingate 1997).

Although plasters and plastering are related to the internal works of buildings in general, renders are the finishing materials of the external surfaces of buildings.

Despite their respective places in the building, plasters and renders have similar functions (Holmes and Wingate 1997, Watts 2001, Seeley 1995).

Functions of plasters and renders in buildings can be summarized as below:

- Conceal irregularities of surfaces and provide a smooth finishing which is suitable for painting or decoration (Seeley 1995, Watts 2001),
- Provide protection against water and moisture penetration, wetting and drying cycles, freezing and thawing cycles, salt crystallization, and biological growths,
- Provide high resistance to impact damages and mechanical abrasions (Seeley 1995, Watts 2001, Matero 1995),
- Improve fire resistance (Seeley 1995, Watts 2001),
- Provide thermal and sound insulation ,
- Modify/Increase sound absorption,
- Easily repaired if damaged (Seeley 1995, Watts 2001, Holmes and Wingate 1997).

Plasters and renders are applied on the surface when they are wet enough. For a successful application, they must have good plasticity and adhesion (Matero 1995). The setting of the plasters is related to raw material compositions and environmental conditions such as temperature and humidity (Matero 1995).

Raw materials of the plasters and renders must be chosen via considering the function and environmental conditions of the building. Most common raw materials used in plasters are mud, gypsum, lime, cement, aggregates and fibrous materials.

2.2. Raw Materials of Plasters Used in Historic Buildings

2.2.1. Mud and Gypsum Plasters

Mud mortars and plasters made by mixing clay, sand, silt and fibrous materials with water have been used since ancient times (Pearson 1994, Caron 1988). Mud materials were generally used in regions in which timber or stone could be found scarcely in Turkey (Eriç 1980). They were, as well, ideal building materials for severe climatic conditions of summer and winter due to their thermal insulation characteristics (Eriç 1980). It is known that mud was used in ancient settlements such as Çatalhöyük, Hacılar, Beycesultan (5900-4000 BC), Troy (2300-1200 BC), Alişar and Boğazköy (1900-1200 BC) (Eriç 1980). Although, they are easily eroded by the action of water, nowadays their usage is becoming important due to the given concern about environmental protection.

Another binding material used in the preparation of plasters and mortars is calcium sulphate hemihydrate ($CaSO_4$. 0.5 H_2O). It is produced by heating gypsum at temperatures between 135 and 175 °C (Reaction I). Hemihydrate transforms into gypsum when mixed with water and set rapidly (Reaction II).

$$CaSO_4 . 2\,H_2O + Heat \rightarrow CaSO_4 . \tfrac{1}{2}\,H_2O + 1.5\,H_2O \qquad \textit{(I)}$$

$$CaSO_4 . \tfrac{1}{2}H_2O + 1.5\,H_2O \rightarrow CaSO_4 . 2\,H_2O \qquad \textit{(II)}$$

Solubility of gypsum is 0.241 grams in 100 ml water at 25°C (Weast and Astle, 1982-1983). Hence, it is not resistant against water. Due to its high solubility, gypsum plasters had been used generally in interior spaces of the buildings (Livingston et. al. 1991).

In ancient Egypt, gypsum mortars were used as a lubricant for placement of (Davey 1961). Also, gypsum mortars were used for over 4000 years at the Middle East (Davey 1961).

2.2.2. Lime Plasters

Lime has been widely used as the binding material in the manufacturing of historic mortars and plasters since Roman times. Limestones which can be classified according to their location, mineralogical and chemical compositions are the raw materials of lime (Schaffer 2004). Finding a suitable lime stone quarry, mining and carrying them to kilns are the first steps for producing lime.

Vitruvius who lived at nearly 90-20 BC in Roman period had pointed out some properties of limestone that would be used in mortar and plaster manufacturing (Vitruvius 1960). He mentioned that less porous and stiff limestones were appropriate to manufacture of lime for mortars while the lime produced from porous ones were appropriate for plasters.

In the 18th century, Belidor stated that "in order to obtain good lime, very hard, heavy and white lime stones ought to be used; so that no lime is so good as that which may be made from white marble. He further observes, limestone fresh quarried is better than that which has been kept in heaps; and that the stone of moist and shaded quarries is better than that of dry ones." (Pasley 1997).

The first step of manufacturing lime is calcination of limestones which are consisted of calcium carbonate ($CaCO_3$). Calcination temperature of calcium carbonate is 900 °C at an environment containing 100 % carbon dioxide (CO_2) and under 760 mm. Hg pressure (Boynton 1980). The calcination temperature decreases with decreasing CO_2 concentration.

During the calcination period, calcium carbonate is transformed into calcium oxide (quicklime) after driven off carbon dioxide gas from the structure (Reaction III).

$$\left.\begin{array}{lll} CaCO_3 + \text{Heat} & \rightarrow & CaO + CO_2 \\ \text{Calcium Carbonate} & & \text{Quicklime} \end{array}\right\} \textit{Calcination} \qquad \textbf{\textit{(III)}}$$

To form lime ($Ca(OH)_2$), quicklime must be mixed and react with water (Reaction IV) (Boynton 1980, Oates 1998). The reaction is exothermic and the process is known as slaking.

$$\left.\begin{array}{lll} CaO + H_2O & \rightarrow & Ca(OH)_2 + \text{Heat} \\ \text{Quicklime} & & \text{Lime} \end{array}\right\} \textit{Slaking} \qquad \textbf{\textit{(IV)}}$$

It had been known from Roman period to present that; for a good slaking, lime should be kept for several years without a contact to air. In Roman period, it had been stated that lime should be used after keeping it for at least three years (Peter 1850). Vitruvius pointed out that lime should be kept for a long time to get its heat off and to provide an entire slaking (Vitruvius 1960). Otherwise, slaking was completed in plasters and cracks started to form (Vitruvius 1960). Plasticity and water absorption capacity of lime increase by time in water (Cowper 1998).

Limes are classified according to impurities they contain (Edwin and Eckel 1928). Lime which contains less than 5 % silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3) can be named as fat (rich or high-calcium) lime. Lime containing more than 5 % silicon dioxide and aluminium oxide can be classified as poor (lean) lime. If lime contains more than 5 % magnesium oxide (MgO) it is named as magnesian lime.

Hydraulic lime is manufactured from limestones which contain high amounts of clay substances. At the temperatures between 950°C and 1250°C, calcium oxide reacts with clay substances; and calcium aluminium silicates are formed. Durability of mortars and plasters prepared by using hydraulic lime is higher than the ones prepared with pure lime (Edwin and Eckel 1928).

Slaked lime hardens by carbonation which takes place slowly absorbing carbondioxide in the atmosphere (Reaction V).

$$\left.\begin{array}{ll} Ca(OH)_2 + CO_2 \rightarrow & CaCO_3 + H_2O \\ \text{Slaked Lime} & \text{Calcium Carbonate} \end{array}\right\} \textit{Carbonation} \qquad \textit{(V)}$$

Most important factors affecting the carbonation of lime are amount of water, concentration of carbon dioxide and permeability of lime (Van Balen and Van Gemert 1994).

Carbonation begins from the outer surface of lime towards the inner surface and proceeds very slowly in the absence or in the presence of high amount of water (Swenson and Sereda 1968). Carbonation increases with the increase of carbon dioxide concentration.

Lime plasters should be produced by mixing lime with aggregates to increase durability and to prevent crack formation (Holmes and Wingate 1997).

Aggregates can be classified as inert and pozzolanic aggregates (Lea 1940). Inert aggregates which contain inactive silicate and aluminate do not react with lime.

However, pozzolanic aggregates contain active silicates and aluminates that react with lime (Lea 1940). Pozzolanic aggregates can be classified as natural and artificial (Lea 1940). Natural pozzolans are generally volcanic in origin (Lea 1940). They are found near the volcanic mountains and in the lake beds near volcanoes. Artificial pozzolans like bricks and tiles are manufactured by heating clayey materials at low temperatures (T<900 °C) (Baronio and Binda 1997).

It is well known that the use of fine powdered natural or artificial pozzolans increases the hydraulicity of mortars and plasters since Roman period. Vitruvius had mentioned importance of using natural pozzolans found around Baiae (an ancient city of Campania) and cities around Mount Vesuvio. Many Roman period monuments had been constructed by using mortars prepared with pozzolans provided from Pozzuoli close to Mount Vesuvio. Most important of these monuments are Pantheon and Colosseum in Rome (Adam 1994). Mortars and plasters of some ancient Greek period monuments were prepared by using volcanic tuffs brought from Santorini (Thera) Island. In some of the Seljuk monuments mortars and plasters, natural pozzolans containing opal-A were used as pozzolanic aggregates to obtain hydraulic mortars and plasters (Tunçoku 2004, Caner 2003).

2.2.2.1. Horasan Plasters

Lime mortars and plasters are classified as non-hydraulic and hydraulic (Holmes and Wingate 1997) (Figure 2.1).

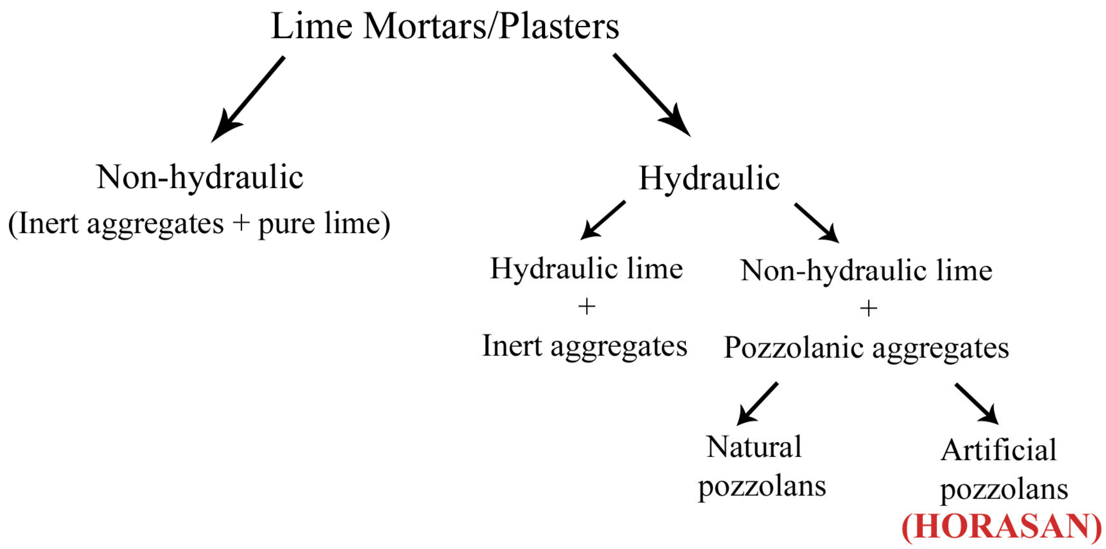


Figure 2.1. Classification of lime mortars and plasters

Non-hydraulic lime mortars and plasters are produced by mixing inert aggregates with pure lime. They harden by reaction of lime with CO_2 in the air. Lime/aggregate ratio, particle size distribution of aggregates, mixing and thickness of the plasters affect the carbonation reaction. Carbonation occurs slowly when high amount of lime is used (Moorehead 1986, Schaffer and Hildsdorf 1993). Some of the additives like blood, egg, cheese, casein, manure, animal glue and plant juices provide a faster hardening to plasters or mortars, increase durability and plastic character of lime and prevent shrinkage (Sickels 1981).

Hydraulic mortars and plasters are manufactured by the use of hydraulic lime, or by mixing pozzolanic aggregates with pure lime (Lea 1940). They are hardened by both the carbonation of lime and the reaction between lime and pozzolans. The reaction products are calcium silicate hydrates and calcium aluminate hydrates, which give high strength to the lime mortars (Lea 1970).

The mortars and plasters made by mixing crushed bricks as artificial pozzolans with lime set in the presence of water and have high mechanical strength (Lea 1940). Due to their setting in water and owing to high mechanical strength, these mortars and plasters have been used in the construction of aqueducts, bridges, and bath buildings since Roman times. They were also used as paving layer on floors and terraces (Bugini et. al. 1993) and a supporting material for mosaics.

Crushed bricks are called as “Horasan” in Turkey (Akman et. al. 1986), “Surkhi” in India (Spence 1974), “Homra” in Arabic countries (Lea 1940) and “Cocciopesto” (Massazza and Pezzuoli 1981) in Roman.

The importance of the use of crushed brick aggregates has been known since Roman period. Vitruvius stated that the crushed bricks should be used instead of sand in the first plaster layers of the walls subjected to high humidity (Vitruvius 1960). He also remarked that natural pozzolans from Cumae should be used in mortars which were directly subjected to water like in aqueducts, breakwaters and dockyards.

Some characteristics of brick aggregates used in the mortars and plasters were mentioned and discussed throughout eighteenth and nineteenth centuries in England and France (Pasley 1997).

In 1744, Loriot asserted that mortars which were prepared with calcined clays ground to powder instead of brick dust and lime set much quicker, and they would be perfect waterproof materials for the lining of cisterns, the coatings of casemates etc.

He also asserted that adding powdered quicklime to mortars which were made with slaked lime was the most effective method for obtaining a good mortar (Pasley 1997). He defined that the mortars should be composed of one part of finely sifted brick dust, two parts of fine river sand, and slaked lime as old as possible and powdered quicklime as one fourth of the whole amounts of aggregates. He suggested that the mortars should be well mixed and used as soon as possible. Otherwise, their application would be imperfect or impossible (Pasley 1997).

However, Higgins and Rondelet quoted but disapproved the method of Loriot. They pointed out that mortar set very quickly with the amount of lime increased by the addition of powdered quicklime but it lost its superiority after a certain period of time while common mortars acquired consistency and hardness equal to hard stones in this period (Pasley 1997).

In 1824, White stated that the difficulty of producing artificial pozzolan since a perfect mortar could not be obtained if the burning of the clay was such as to cause vitrification. He defined that the use of pozzolans and lime in the lime/pozzolan proportions between 1/3 and 1/4 obtain all the advantages of good building cement (Pasley 1997). He also mentioned that pozzolans should be finely powdered in order to provide good adhesion with lime.

Vicat (1818, 1828) gave recommandations about firing processes about clays (Vicat 2003). According to him, clays could be fired by three methods.

In the first method;
"previously pulverizing the substance, and spreading it out in a layer one centimetre, or about a tenth of an English inch thick, on an iron plate brought to a red heat, and subjecting it to the same heat for 20 or 25 minutes, stirring the powder continually in the mean time, that every may be equally acted upon.".

In the second method which was only suitable for small scales;
"making the substance porous by mixing it up after pulverizing it, into a stiff paste, with combustible substances in a state of minute division, such as saw-dust, chopped straw, and burning it when dry enough, in the upper part of a lime kiln, or where the heat is moderate."

In the third method;
"If these methods cannot be used, he recommends burning the substance in its natural state, but with the precaution of first breaking it into small pieces less than a man's fist, exposed to air and with moderate heat."

Furthermore, Vicat expressed the pozzolanic activities of clays due to these firing processes as follows;

"very fine and soft clay composed of mainly silica and alumina whether it contain little or much oxide of iron, or little or much carbonate of lime, will make a very energetic artificial pozzolana, if burned by the two first methods, but only an energetic one if burned by the third method, and if burned to the hardness of strong bricks, it will form one of little energy". According to him, "in order to obtain hydraulic mortars capable of acquiring great hardness under water, or under ground, or in situations always moist, weak hydraulic limes must be combined with energetic pozzolanas, that hydraulic limes may be combined with puzzolanas of little energy".

In 1829, Tressuart stated that "bricks, which in burning have had a strong current of air passing through them, make a better artificial puzzolana, than bricks of the same earth equally well burned but not subject to air during this" (Pasley 1997).

In the specification of Ottoman period, the use of new and well fired bricks was suggested in horasan mortars and plasters making (Akman 1986, Denel 1982). This shows that probably crushed brick aggregates of horasan mortars and plasters were not obtained from old building bricks; they might be manufactured intentionally.

The raw materials used in the production of bricks are natural clays containing quartz, feldspar and other secondary minerals. The function of clay minerals is to provide plasticity while feldspars decrease the melting point and quartz fills the spaces in the bricks.

Manufacturing of bricks starts with removing stone pieces from the natural clay source and then mixed with water. The plastic mixture is then shaped, dried and heated. Heating destroys the crystal structure of clays, and pozzolanic amorphous structures formed when the heating temperature is between 600 and 900 ºC (Baronio and Binda 1997). At temperatures over 900 ºC pozzolanic characteristic is lost due to the formation of stable minerals like mullite, cristobalite etc. (Baronio and Binda 1997, Sujeong 1999).

Amorphous substances are aluminosilicates which react with lime and form insoluble calcium silicate hydrate and/or calcium aluminate hydrate at brick-lime interfaces and the pores of brick aggregates. For instance; amorphous metakaolin (Al_2O_3. $2SiO_2$) which is produced from the kaolinite (Al_2O_3. $2SiO_2$. $2H_2O$) (Reaction I) reacts with lime ($Ca(OH)_2$) in the presence of water (H_2O) and form calcium silicate hydrate ($3CaO.2SiO_2.7H_2O$) and tetracalcium aluminate hydrate ($4CaO.Al_2O_3.19H_2O$) (Reaction II) (Prince et. al. 2001).

$$\text{“}\underset{\text{Kaolinite}}{Al_2O_3.\ 2SiO_2.\ 2H_2O} \rightarrow \underset{\text{Metakaolin}}{Al_2O_3.\ 2SiO_2} + 2H_2O\text{”} \qquad \textbf{\textit{(I)}}$$

$$\text{“}\underset{\text{Metakaolin}}{Al_2O_3.\ 2SiO_2} + \underset{\text{Lime}}{7Ca(OH)_2} + \underset{\text{Water}}{19H_2O} \rightarrow \underset{\text{Tetracalcium aluminate hydrate}}{4CaO.Al_2O_3.19H_2O} + \underset{\text{Calcium silicate hydrate}}{3CaO.2SiO_2.7H_2O}\text{”} \qquad \textbf{\textit{(II)}}$$

Formation of these products gives the hydraulic character to horasan mortars and plaster and improves their strength. This may explain the use of brick-lime mortars and plasters in construction of many historic buildings since ancient times (Moropoulou et. al. 2002a).

In the recent studies, hydraulic properties, raw material compositions, mineralogical and microstructural characteristics of horasan mortars and plasters of the different historic buildings were determined in order to understand their technology and to produce repair mortars and plaster compatible with the existing ones (Moropoulou et. al. 1996, Moropoulou et. al. 2002a, Moropoulou et. al. 2000b, Bakolas et. al. 1998, Biscontin et. al. 2002, Bugini et. al. 1993). Investigated mortars and plasters revealed different binder/aggregate ratios varying from 1/4 to 1/2. Binders were mostly composed of calcite due to carbonated lime and calcium silicate hydrates and calcium aluminate hydrates which are formed as a result of the reaction between lime and brick aggregates.

There are few studies on the determination of pozzolanicities of the historic bricks. These studies indicated that bricks must have a high amount of clay minerals and must be fired at low temperatures of (600-900 °C) to have pozzolanicity (Baronio and Binda 1997, Böke et. al. 2004). These results show that not all the historic bricks have pozzolanic properties although fired at low temperatures (Baronio and Binda 1997, Baronio et. al. 1997, Böke et. al. 2004).

In Turkey, there are few studies on raw material compositions, basic physical, mineralogical, microstructural and hydraulic properties of horasan mortars and plasters which were used mainly in historic baths. The results of these studies indicated that the mortars and plasters used are hydraulic and this is provided by the use of pozzolanic bricks (Akman et. al. 1986, Şatongar 1994, Güleç and Tulun 1996, Böke et. al. 1999, Böke et. al. 2004).

CHAPTER 3

EXPERIMENTAL METHODS

In this study, horasan plasters and lime plasters collected from three Ottoman bath buildings located in Urla-Seferihisar region were analyzed in order to determine their raw material compositions, basic physical, mineralogical, microstructural and hydraulic properties. Mineralogical and chemical compositions, microstructures, morphologies and pozzolanicities of the brick powders and fragments used as aggregates in the plasters were also examined to find out the relationship between hydraulic properties of the plasters and the bricks. Bricks used in the construction of the baths were also analyzed to compare their characteristics with the ones used in the plasters.

3.1. Sampling

Horasan plaster samples were collected from the different spaces and levels of Hersekzade, and Kamanlı Baths built in Urla and Düzce Bath built in Seferihisar. These baths are located very close to each other and have similar construction techniques (Reyhan 2004).

Hersekzade Bath is a 15th Century Ottoman Bath located in the centre of Urla (Figure 3.1, Reyhan 2004).

Figure 3.1. Hersekzade Bath, southeast and northeast elevations

Kamanlı Bath is a 15th century Ottoman Bath located at the Kamanlı site of Urla (Figure 3.2, Reyhan 2004).

Figure 3.2. Kamanlı Bath, north and south elevations

Düzce (Hereke) Bath is a 16th century Ottoman bath located in Düzce Village of Seferihisar (Figure 3.3, Reyhan 2004).

Figure 3.3. Düzce Bath, northeast and northwest elevations

Horasan and lime plaster samples were taken from soyunmalık (disrobing area), ılıklık (warm area), sıcaklık (hot area) and halvet spaces of the baths. Bricks were collected from the domes of the baths. Relatively sound samples were taken from parts of the walls that were not subjected to deterioration problems (Figure 3.4-3.9).

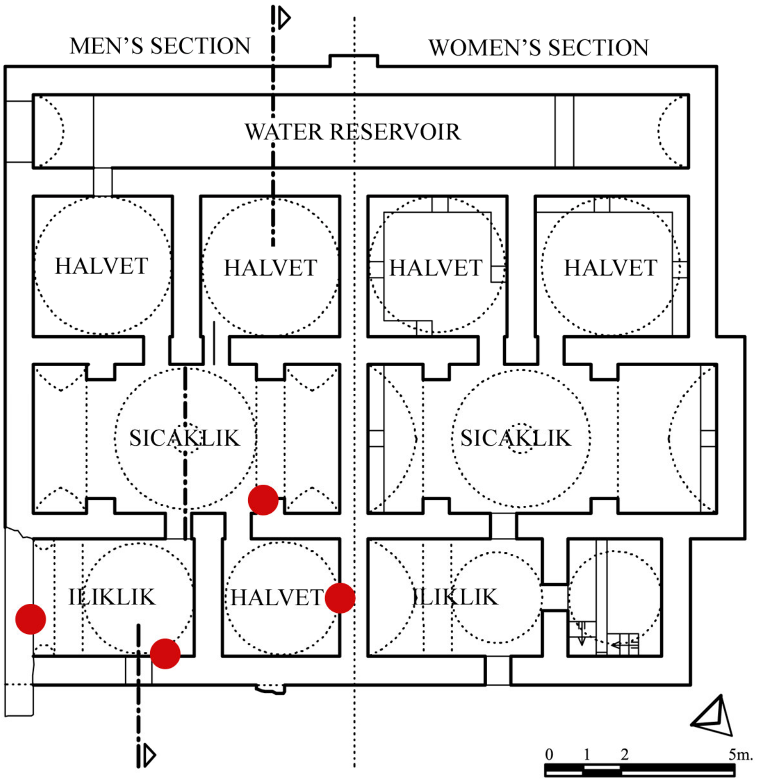


Figure 3.4. Plan of Hersekzade Bath showing where the samples were collected (Source: Reyhan 2004)

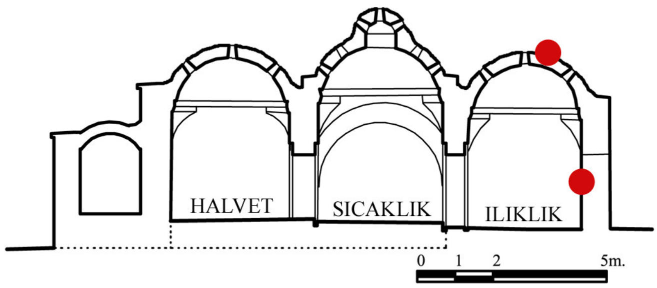


Figure 3.5. Section of Hersekzade Bath showing where the samples were collected (Source: Reyhan 2004)

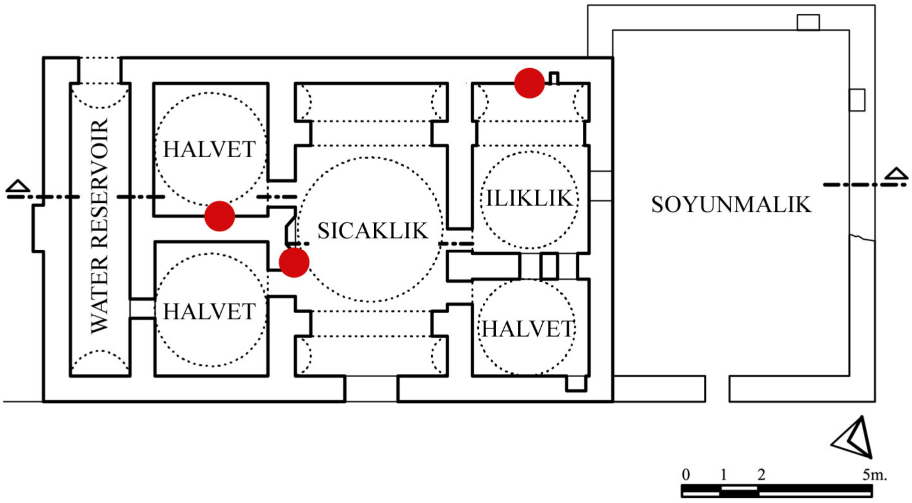


Figure 3.6. Plan of Kamanlı Bath showing where the samples were collected (Source: Reyhan 2004)

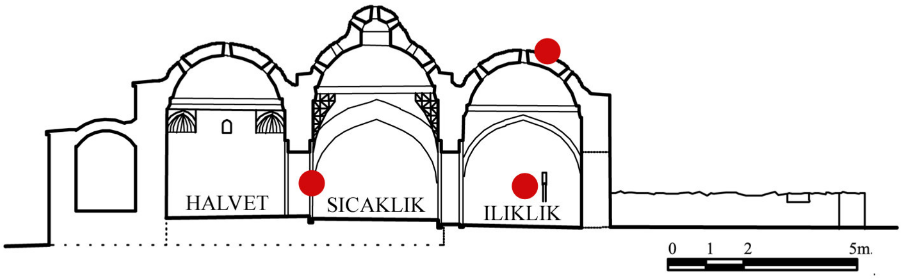


Figure 3.7. Section of Kamanlı Bath showing where the samples were collected (Source: Reyhan 2004)

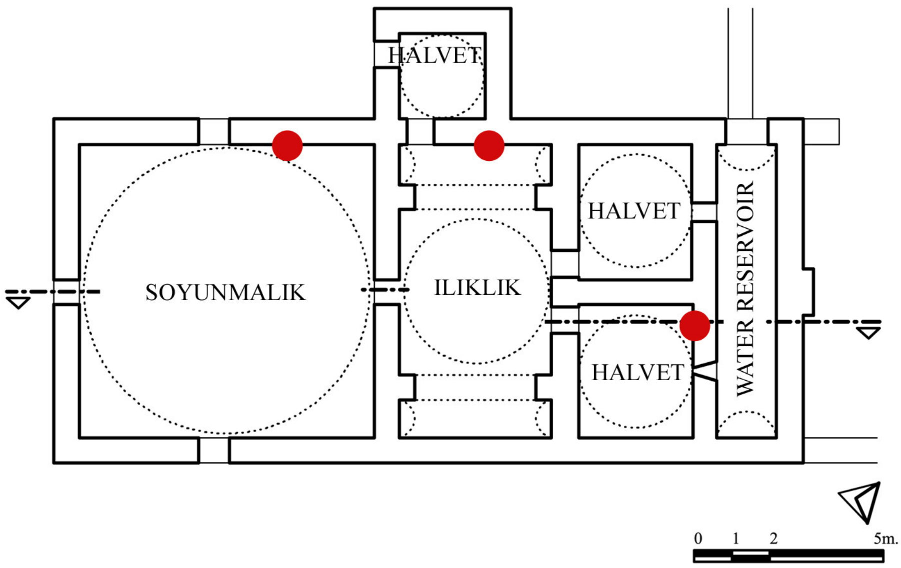


Figure 3.8. Plan of Düzce Bath showing where the samples were collected (Source: Reyhan 2004)

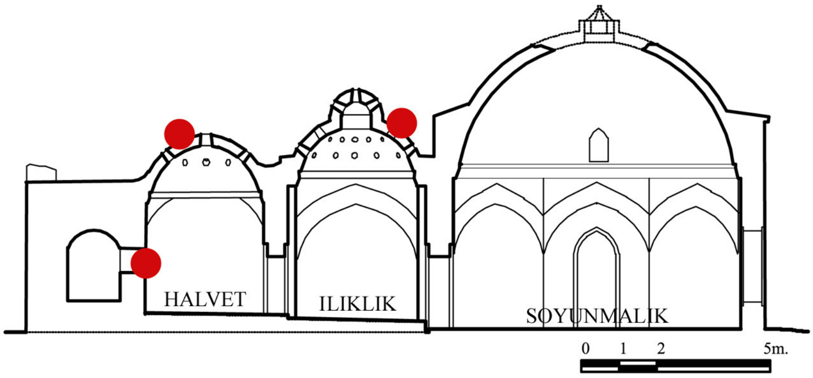


Figure 3.9. Section of Düzce Bath showing where the samples were collected (Source: Reyhan 2004)

On the wall surfaces of the interior spaces of the baths, two levels (a lower level and an upper level) were observed. Lower level plasters were extended to 1.5 m height above the existing floor surface. A clear boundary was visible between lower level and upper level. These levels were composed of different plaster layers and could be distinguished with their different colors.

Lower level plasters were composed of a rough plaster layer with a dark red colored finishing layer (~ 0.3 mm.). The finishing layer contained finely powdered brick aggregates. These types of plasters were used in soyunmalık, ılıklık and sıcaklık spaces of the baths. Unlikely, two rough horasan plaster layers and a very thin finishing layer were observed in halvet spaces.

Upper level plasters were generally composed of a rough horasan plaster layer with a fine lime plaster layer (Table 3.1).

Samples were collected both lower and upper levels since there was a great possibility that the lower level plaster surfaces, which were more vulnerable to chemical and physical action of water, could be prepared as waterproof.

Table 3.1. Table showing the levels, layer numbers of plasters according to the spaces and the baths

	SOYUNMALIK								ILIKLIK								SICAKLIK								HALVET								
	Lower Level				Upper Level				Lower Level				Upper Level				Lower Level				Upper Level				Lower Level					Upper Level			
	Hor.		Lime		Hor.		Lime		Hor.		Lime		Hor.		Lime		Hor.		Lime		Hor.		Lime		Hor.			Lime		Hor.		Lime	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	3	1	2	1	2	1	2
Hersekzade Bath	DOES NOT HAVE A SOYUNMALIK SPACE.								●	-	-	-	●	-	-	-	●	-	-	-	●	-	●	-	●	-	-	-	-	●	-	-	-
Kamanlı Bath	DOES NOT HAVE A SOYUNMALIK SPACE.								●	-	-	-	●	-	●	-	●	∗	-	-	●	-	●	-	●	●	∗	-	-	●	-	●	-
Düzce Bath	●	●	-	-	●	-	●	●	●	-	-	-	●	●	●	-	DOES NOT HAVE A SICAKLIK SPACE.								●	●	∗	-	-	●	∗	∗	-

∗ Intervention plaster

In Hersekzade Bath, both lower level and upper level plasters of the spaces were composed of a single horasan plaster layer, with the exception of the upper level of the sıcaklık space which was consisted of a horasan plaster layer with a lime plaster layer (Table 3.1). In addition to the plaster layers, there was a very thin, dark red colored finishing layer on the horasan plasters of lower levels of sıcaklık and halvet spaces. The thicknesses of the lower level horasan plasters were approximately 1.5 cm. while the thicknesses of the upper level horasan plasters were between 0.8-1.5 cm. Horasan plasters with two layers were applied on the dome walls of ılıklık space. The thickness of the first layer was approximately 2.5 cm. and the second layer was 1.2 cm. (Figure 3.10, 3.11 and 3.12).

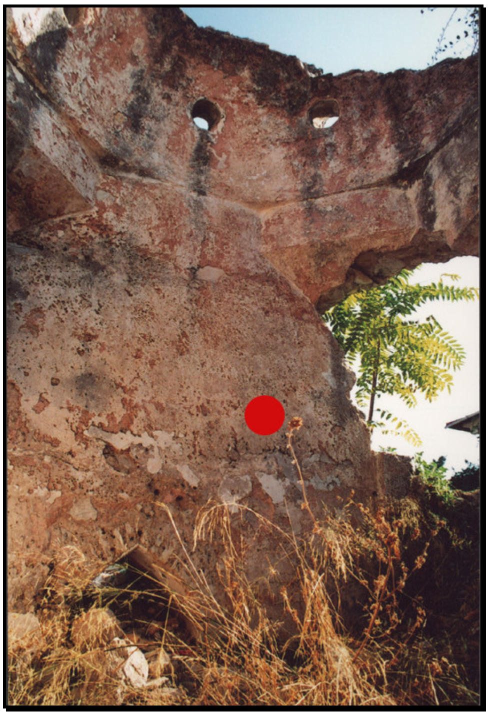


Figure 3.10. Hersekzade Bath, ılıklık space, showing where the samples were collected

Figure 3.11. Hersekzade Bath, sıcaklık space, showing where the samples were collected

Figure 3.12. Hersekzade Bath, halvet space, showing where the samples were collected

In Kamanlı Bath, the upper level plasters of all of the spaces were composed of a horasan plaster layer with a lime plaster. The lower level of the ılıklık space was composed of a single horasan plaster layer while the sıcaklık space was composed of two horasan plaster layers and the halvet space three horasan plaster layers. But, it was thought that the last layers of the sıcaklık space and the halvet space must be intervention plasters since the dark red colored finishing layers were under these last layers (Table 3.1). The thicknesses of the first layers of lower level horasan plasters varied in the range of 0.8-1.5 cm.. The thicknesses of the second and third plasters layers were about 0.8 cm. and 0.5 cm. The thicknesses of the upper level horasan plasters were in the range of 1.0-1.5 cm. and the thicknesses of the lime plasters ranged between 0.3-0.8 cm. (Figure 3.13, 3.14, 3.15).

Figure 3.13. Kamanlı Bath, ılıklık space, showing where the samples were collected

Figure 3.14. Kamanlı Bath, sıcaklık space

Figure 3.15. Kamanlı Bath, halvet space, showing where the samples were collected

In Düzce Bath, the numbers of plaster layers differentiated according to the spaces. The lower level was composed of two horasan plaster layers in the soyunmalık space, a single horasan plaster layer in the ılıklık space and three horasan plaster layers in the halvet space. The upper level was composed of a horasan and two lime plaster layers in soyunmalık space while two horasan and a lime plaster layers in ılıklık and halvet spaces (Table 3.1). On the top horasan plaster layers of the soyunmalık and the ılıklık space, there was a very thin, dark red colored finishing layer.

The top horasan plaster layer of the lower level of the halvet space was thought as an intervention plaster since the original finishing layer is under it.

The second horasan plaster layer and the lime plaster layer of the upper level of the halvet space were also thought as intervention plasters since there was a very thin carbonated lime layer between the first horasan plaster layer and the second horasan plaster layer (Böke et. al. 2004).

The thicknesses of the lower level horasan plasters were varied between 1.0-2.0 cm. for the first layers and 0.8-1.0 cm. for the second layers while the third layer was close to 0.5 cm.

The thickness of the first layer horasan plaster of the upper levels was 0.8 cm. for the ılıklık space and 1.3 cm. for the halvet space while the second layer horasan plaster was 1.4 cm. for the ılıklık space and 0.4 cm. for the halvet space (Figure 3.16, 3.17, 3.18).

Figure 3.16. Düzce Bath, soyunmalık space, showing where the samples were collected

Figure 3.17. Düzce Bath, ılıklık space, showing where the samples were collected

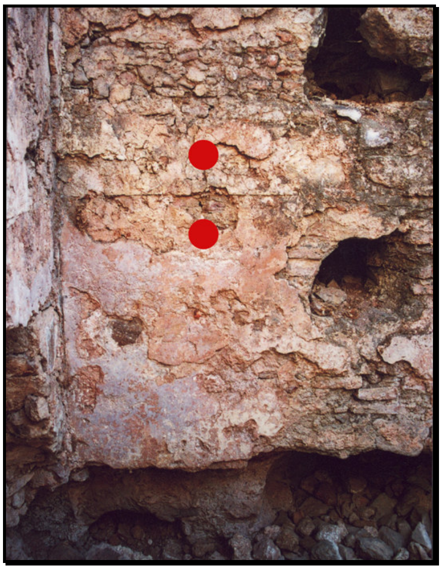


Figure 3.18. Düzce Bath, halvet space, showing where the samples were collected

Samples were labeled according to the bath, space and level, and the type of plaster and the layer of the sample (if exists). In labeling;

- First letter shows the name of the bath (Hersekzade:H, Kamanlı:K, Düzce:D).
- Second letter shows the name of the space or the architectural element (Ilıklık: I, Soyunmalık: So, Sıcaklık: S, Halvet:H, Dome:D).
- Third letter shows the level of the sample (Lower level:L, Upper level:U).
- Fourth letter shows the type of the sample (Lime plaster:L, Brick:Br). Horasan plasters are not shown by any letter.
- Number shows the layer of the sample if exists.

Labels and definitions of the samples are given as following:

Table 3.2. Definitions of the samples collected from Hersekzade Bath located in Urla

Hersekzade Bath in Urla	
Sample	**Definition**
Plasters collected from the ılıklık space	
H.I.D.1	First layer of the horasan plaster collected from the dome of the ılıklık space
H.I.D.2	Second layer of the horasan plaster collected from the dome of the ılıklık space
H.I.L	Horasan plaster collected from the lower level of the ılıklık space
H.I.U	Horasan plaster collected from the upper level of the ılıklık space
Plasters collected from the sıcaklık space	
H.S.L	Horasan plaster collected from the lower level of the sıcaklık space
H.S.U	Horasan plaster collected from the upper level of the sıcaklık space
H.S.U.L	Lime plaster collected from the upper level of the sıcaklık space
Plasters collected from the halvet space	
H.H.U	Horasan plaster collected from the upper level of the halvet space
H.H.L	Horasan plaster collected from the lower level of the halvet space
Bricks collected from the building	
H.Br	Brick collected from the dome of the ılıklık space

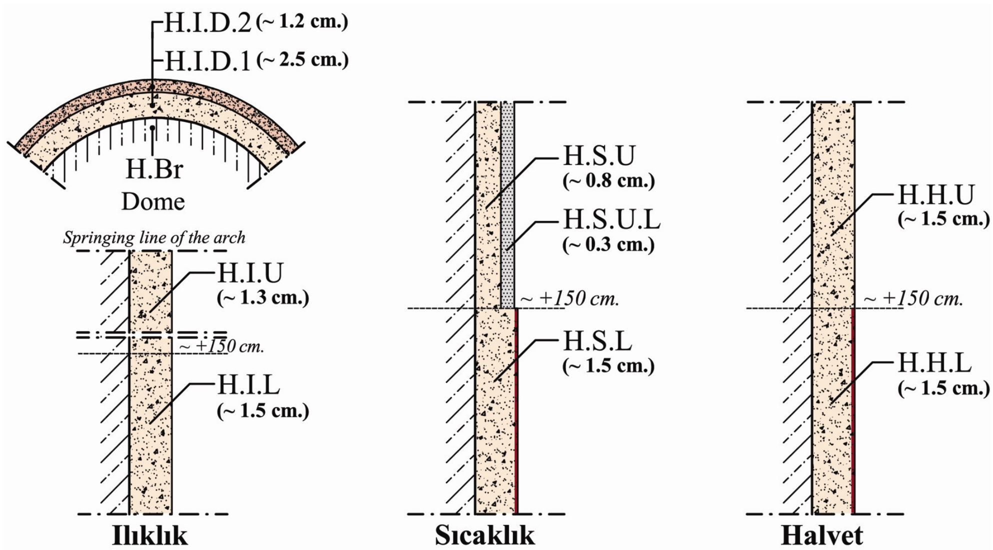


Figure 3.19. Illustrative drawing showing the plaster layers of Hersekzade Bath

Table 3.3. Definitions of the samples collected from Kamanlı Bath located in Urla

Kamanlı Bath in Urla	
Sample	**Definition**
Plasters collected from the ılıklık space	
K.I.L	Horasan plaster collected from the lower level of the ılıklık space
K.I.U	Horasan plaster collected from the upper level of the ılıklık space
K.I.U.L	Lime plaster collected from the upper level of the ılıklık space
Plasters collected from the sıcaklık space	
K.S.L.1	First layer of the horasan plaster collected from the lower level of the sıcaklık space
K.S.L.2	Second layer of the horasan plaster collected from the lower level of the sıcaklık space
K.S.U	Horasan plaster collected from the upper level of the sıcaklık space
K.S.U.L	Lime plaster collected from the upper level of the sıcaklık space
Plasters collected from the halvet space	
K.H.L.1	First layer of the horasan plaster collected from the lower level of the halvet space
K.H.L.2	Second layer of the horasan plaster collected from the lower level of the halvet space
K.H.L.3	Third layer of the horasan plaster collected from the lower level of the halvet space
K.H.U	Horasan plaster collected from the upper level of the halvet space
K.H.U.L	Lime plaster collected from the upper level of the halvet space
Bricks collected from the building	
K.Br	Brick collected from the dome of the ılıklık space

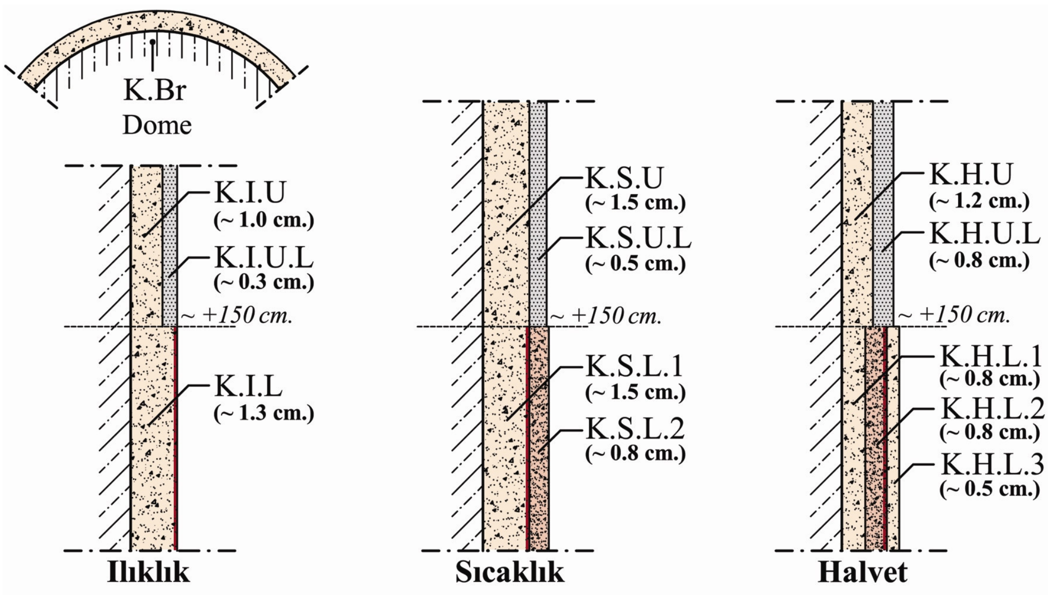


Figure 3.20. Illustrative drawing showing the plaster layers of Kamanlı Bath

Table 3.4. Definitions of the samples collected from Düzce (Hereke) Bath located in Seferihisar

Düzce (Hereke) Bath in Seferihisar	
Sample	**Definition**
Plasters collected from the soyunmalık space	
D.So.L.1	First layer of the horasan plaster collected from the lower level of the soyunmalık space
D.So.L.2	Second layer of the horasan plaster collected from the lower level of the soyunmalık space
D.So.U.L.1	First layer of the lime plaster collected from the upper level of the soyunmalık space
D.So.U.L.2	Second layer of the lime plaster collected from the upper level of the soyunmalık space
Plasters collected from the ılıklık space	
D.I.L	Horasan plaster collected from the lower level of the ılıklık space
D.I.U.1	First layer of the horasan plaster collected from the upper level of the ılıklık space
D.I.U.2	Second layer of the horasan plaster collected from the upper level of the ılıklık space
D.I.U.L	Lime plaster collected from the upper level of the ılıklık space
Plasters collected from the halvet space	
D.H.L.1	First layer of the horasan plaster collected from the lower level of the halvet space
D.H.L.2	Second layer of the horasan plaster collected from the lower level of the halvet space
D.H.L.3	Third layer of the horasan plaster collected from the lower level of the halvet space
D.H.U.2	Second layer of the horasan plaster collected from the upper level of the halvet space
D.H.U.1	First layer of the horasan plaster collected from the upper level of the halvet space
D.H.U.L	Lime plaster collected from the upper level of the halvet space
D.H.D	Horasan plaster collected from the dome of the halvet space
Bricks collected from the building	
D.Br	Brick collected from the building

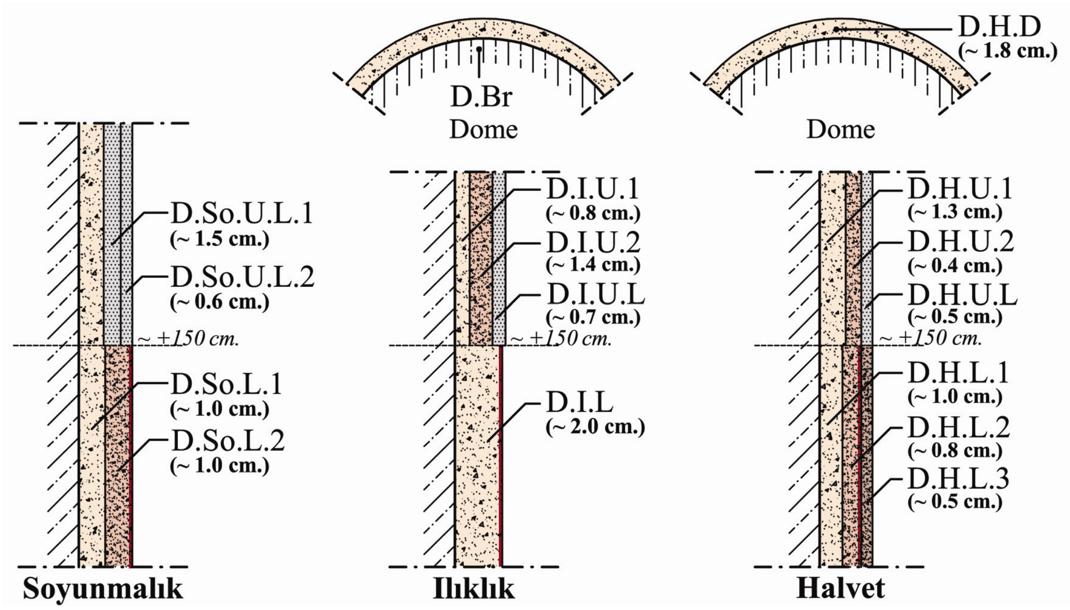


Figure 3.21. Illustrative drawing showing the plaster layers of Düzce Bath

3.2. Experimental Study

Experimental study includes determination of the following properties of horasan plasters, crushed bricks used as aggregates in the horasan plasters, lime plasters, and building bricks.

They are,

- Basic physical properties; the densities and porosities of plasters and building bricks,
- Raw material compositions; binder/aggregate ratios of plasters and particle size distributions of the aggregates,
- Hydraulicity; due to the weight losses occurs between 200-600ºC and 600-900ºC in the plasters,
- Mineralogical and chemical compositions and microstructural properties of horasan plasters, crushed bricks used as aggregates in the horasan plasters; lime plasters and building bricks,
- Pozzolanic activities of the crushed brick aggregates of horasan plasters and building bricks.

3.2.1. Determination of Basic Physical Properties

Bulk densities and porosities of plasters and building bricks were determined by using RILEM standard test methods (RILEM 1980). Density is the ratio of the mass to its bulk volume and is expressed in grams per cubic centimeters (g/cm^3). Porosity is the ratio of the pore volume to the bulk volume of the sample, and is usually expressed in per cent (%).

Measurement of density and porosity was carried out on two samples of each plaster and building brick. Samples were first dried in an oven at low temperatures (40ºC) at least for 24 hours then they were weighed by a precision balance (AND HF-3000G) to determine their dry weights (M_{dry}). Subsequently, they were entirely saturated with distilled water in a vacuum oven (Lab-Line 3608-6CE Vacuum Oven). The saturated weights (M_{sat}) and the Archimedes weights (M_{arch}) that were determined with hydrostatic weighing in distilled water were measured by precision balance. Afterwards, bulk densities (D) and porosities (P) of the plaster and brick samples were calculated by using the formulas given below:

$$D\ (g/cm^3) = M_{dry} / (M_{sat} - M_{arch})$$
$$P\ (\%) = [(M_{sat} - M_{dry}) / (M_{sat} - M_{arch})] \times 100$$

where;

D = Density (g/cm^3)

P = Porosity (%)

M_{dry} = Dry weight (g)

M_{sat} = Saturated weight (g)

M_{arch} = Archimedes weight (g)

M_{sat}-M_{dry} = Pore volume (g)

M_{sat}- M_{arch} = Bulk volume (g)

3.2.2. Determination of Raw Material Compositions of Plasters

Raw material composition analyses were carried out for plasters, in order to determine their lime-aggregate ratios and the particle size distributions of the aggregates.

Binder-aggregate ratios of the plasters were determined by dissolving the carbonated lime ($CaCO_3$) from aggregates (Jedrzejevska 1981). Two samples from each plaster were prepared, dried and weighed (M_{sam}) by a precision balance. Then the dried samples were left in a dilute hydrochloric acid (%5) solution until the carbonated lime dissolved entirely. Insoluble part -which was consisted of aggregates- was filtered, washed with distilled water, dried in an oven and weighed by a precision balance (M_{agg}). Ratios of acid soluble and insoluble parts were calculated by the following formula:

$$\text{Insoluble \%} = [(M_{sam} - M_{agg}) / (M_{sam})] \times 100$$

$$\text{Acid Soluble \%} = 100 - \text{Insoluble \%}$$

where;

M_{sam} = Dry weight of the sample (g)

M_{agg} = Dry weight of the aggregates (g)

Acid soluble ratio does not give the exact lime ratio of the plasters, since it is calculated with the dissolved carbonated lime ($CaCO_3$). The lime ratio must be calculated according to the lime ($Ca(OH)_2$) which had been used during the production process of the plasters.

$$\underbrace{Ca(OH)_2}_{74g} + \underbrace{CO_2}_{44\,g} \rightarrow \underbrace{CaCO_3}_{100g} + H_2O \quad \text{(Molecular weights)}$$

Lime transforms into carbonated lime when it reacts with carbon dioxide (CO_2) in the atmosphere. According to the molecular weights as shown in the equation above, 100 gram carbonated lime derives from 74 gram lime. Therefore, lime/aggregate ratio was calculated as following:

Aggregate % = (100 × Insoluble) / [((Acid Soluble % × $M.W._{Ca(OH)_2}$) / $M.W._{CaCO_3}$) + Insoluble %]

Lime % = 100 – Aggregate %

where;

$M.W._{CaCO_3}$ = Molecular weight of $CaCO_3$ which is 100.

$M.W._{Ca(OH)_2}$ = Molecular weight of $Ca(OH)_2$ which is 74.

Determination of particle size distributions of aggregates was carried out by sieving them through a series of sieves (Retsch mark) having the sieve sizes of 53 µm, 125 µm, 250 µm, 500 µm, 1180 µm by using an analytical sieve shaker (Retsch AS200). Particles remained on each sieve surface were weighed by a precision balance and their percentages were calculated.

3.2.3. Determination of Pozzolanic Activity of Crushed Bricks Used as Aggregates and Building Bricks

Pozzolanic activity of the crushed bricks used as aggregates and the building bricks were determined by using electrical conductivity and measurement of the concentration changes of calcium, potassium and sodium ions by flame photometer methods before and after addition of powdered brick (less than 53 micrometer) into saturated calcium hydroxide solution.

In the first analysis, pozzolanic activity of fine aggregates (less than 53µm size) were determined by mixing them with saturated calcium hydroxide solution ($Ca(OH)_2$) with the solution ratio of 5 g/200ml. In this analysis, at first, electrical conductivity of the saturated calcium hydroxide was measured; and then the decrease in the electrical conductivity of saturated calcium hydroxide mixed with powdered bricks was recorded at the end of two minutes. Their difference (ΔEC in mS/cm) was used to express the pozzolanic activity of the crushed brick aggregates and building bricks. It was suggested that if the ΔEC is over 1.2mS/cm the aggregates has good pozzolanicity (Luxan et al. 1989).

In the second analysis, calcium (Ca), potassium (K) and sodium (Na) ion concentrations of saturated calcium hydroxide solution ($Ca(OH)_2$) was measured by flame photometer. For each sample, 400 ml calcium hydroxide solution was put in a plastic bottle. Then, 1 gram brick powders from each sample were added to the bottles. These mixtures were left at 40 ºC for periods of 8, 16 and 30 days in closed bottles. At the end of each period, calcium, potassium and sodium ion concentrations were measured with flame photometer. The difference in the concentrations of calcium ion was used to compare the pozzolanic activities of the brick powders.

3.2.4. Determination of Mineralogical and Chemical Compositions and Microstructural Properties of Plasters, Crushed Bricks Used as Aggregates and Building Bricks

Mineralogical compositions of horasan plasters, lime plasters, crushed bricks used as aggregates and building bricks were determined by X-ray Diffraction analysis performed by using a Philips X-Pert Pro X-ray Diffractometer. The analyses were performed on finely ground samples of less than 53 µm.

Chemical compositions of horasan plasters, lime plasters, crushed bricks used as aggregates and building bricks were determined by Philips XL 30S-FEG Scanning Electron Microscope (SEM) equipped with X-Ray Energy Dispersive System (EDS). The pellet samples which were prepared by the fine ground powder were used in this analysis.

Microstructural properties were determined by a Philips XL 30S-FEG Scanning Electron Microscope (SEM) and a stereo microscope (Nikon L150).

Atomic force microscope (AFM, Digital instrument, MMSPM-Nanoscope 4) was used in contact mode to study the brick-lime interface in the plaster matrices by generating a map of their topography. The AFM was operated with a 100µm scanning head; its X-Y scan range was 100µm and its Z scan range was 5µm.

3.2.5. Determination of Hydraulicity of Plasters

The hydraulic properties of the plasters were determined by heating the plaster samples in a furnace. In this analysis, one gram fine ground sample was heated in the crucible at 200ºC for 2 hours, at 600ºC for 1 hour and at 900ºC for 1 hour. Weight losses at these temperatures were then precisely measured. Weight loss at 200ºC is due to the loss of hygroscopic (adsorbed) water. Weight loss at 200 to 600ºC is mainly due to the loss of chemically bound water of hydraulic products, such as calcium silicate hydrates and calcium alumina hydrates formed in the plaster samples. Weight loss at temperatures over 600ºC is due to the decomposition of calcium carbonates present as binder in the plasters. If the ratio of CO_2/H_2O (bound) is between 1 and 10, the plasters can be accepted as hydraulic (Bakolas et. al. 1998, Moropoulou et. al. 2000a).

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the experimental results of main characteristics of horasan and lime plasters, brick aggregates in used horasan plasters and building bricks used in the baths were given and discussed.

4.1. Basic Physical Properties of Plasters and Building Bricks

4.1.1. Density and Porosity Values of Horasan Plasters

Density and porosity values of horasan plasters collected from the lower levels of the baths were in the range of 1.2-1.7 g/cm^3 and 31-54 % by volume respectively. Density values of horasan plasters collected from the upper levels were in the range of 1.0-1.6 g/cm^3 and their porosity values varied between 37-48 % (Figure 4.1, 4.2 and 4.3).

Horasan plasters collected from the domes of the baths had density and porosity values ranging between 1.3-1.5 g/cm^3 and 37-47 % respectively (Figure 4.1 and 4.3).

When the density and the porosity values of lower level horasan plasters and upper level ones were compared with each other, it was found that the values were almost in the same ranges.

Density and porosity values of the finishing layers could not be determined by using RILEM standard tests because the finishing layers were so thin to apply this test method. The porosity of the finishing layers was measured by SEM. SEM analyses revealed that finishing layers had 6 % porosity. Detailed results of these analyses will be given in the microstructural property analyses section (4.5.1.1).

Lime plasters applied on upper level horasan plasters had density values ranging between 1.3-1.8 g/cm^3 and porosity values ranging between 25-46 % (Figure 4.1, 4.2 and 4.3).

All these values were almost in the same ranges with other crushed brick-lime mortars and plasters collected from several historic buildings. For instance, density and porosity values of some plaster samples collected from some monuments belonging to different periods in Rhodes varied in the range of 1.3-1.7 g/cm^3 and 26-43 % by volume respectively (Moropoulou et. al. 2000a) while density and porosity values of brick-lime mortars collected some Byzantine monuments were in the range of 1.5-1.6 g/cm^3 and 42-46 % respectively (Moropoulou et. al. 2000c).

Horasan mortars collected from some monuments in İstanbul, had density values of 1.3 g/cm^3 and 1.7 g/cm^3 (Akman et. al. 1986, Şatongar 1994). Horasan plasters collected from some Ottoman bath buildings in Bursa, Edirne and İstanbul had density and porosity values ranging between 1.1-2.1 g/cm^3 and 10-55 % respectively (Böke et. al. 2004, Güleç and Tulun 1996).

4.1.2. Density and Porosity Values of Building Bricks

The average density and porosity values of bricks collected from the domes were found as 1.8 gr/cm^3 and 31 % (Figure 4.1, 4.2 and 4.3). These values were almost in the same ranges with other bricks used in some historic buildings in Anatolia (Böke et. al. 2004, Tunçoku et. al. 1993).

Porosity and density values of bricks depend on their composition, preparation technologies and firing temperatures (Cultrone et. al. 2003). Hence, historic bricks had been manufactured considering their function in the construction (Moropoulou et. al. 2002b). For instance, low dense and high porous bricks were used in the construction of the dome of Hagia Sophia in İstanbul due to the structural necessity (Moropoulou et. al. 2002b).

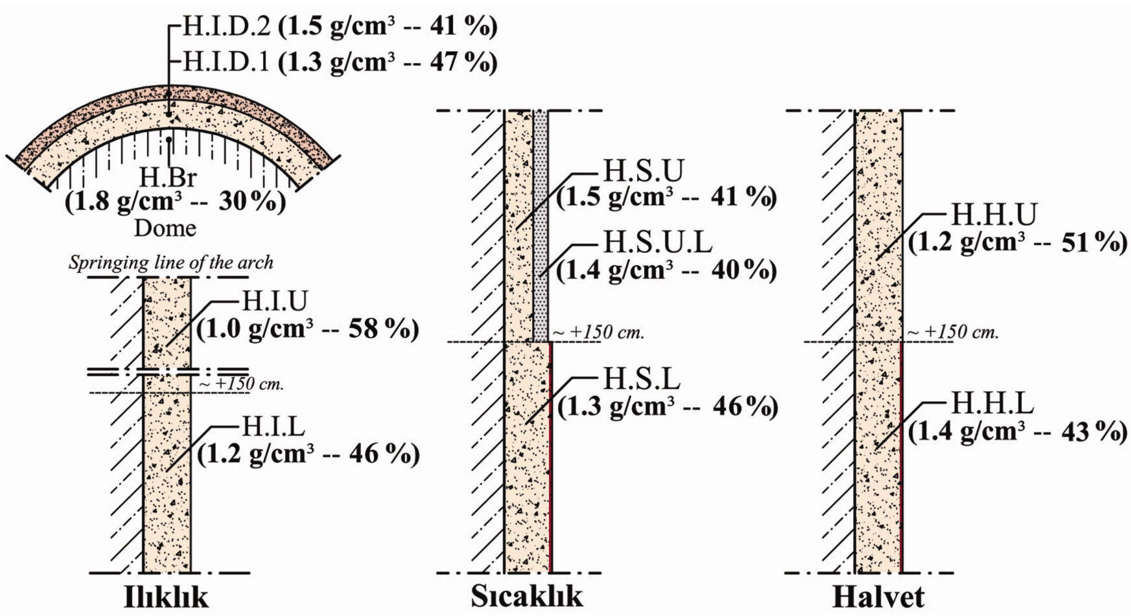


Figure 4.1. Density and porosity values of samples collected from Hersekzade Bath

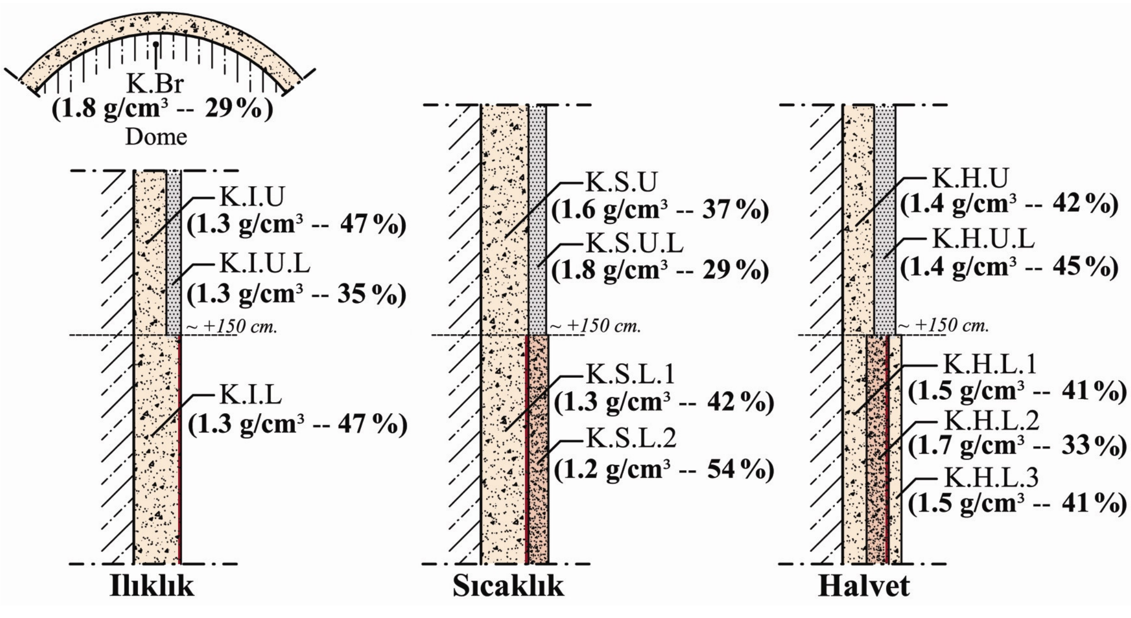


Figure 4.2. Density and porosity values of samples collected from Kamanlı Bath

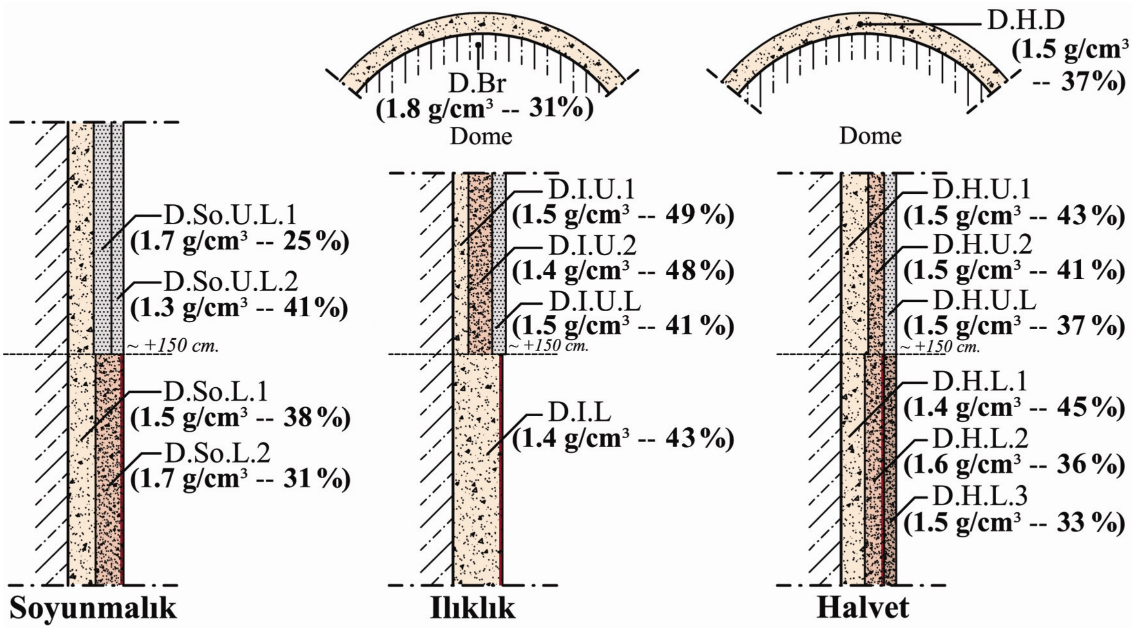


Figure 4.3. Density and porosity values of samples collected from Düzce Bath

4.2. Raw Material Compositions of Plasters

Raw material compositions of plasters were described by lime/aggregate ratios and particle size distributions of aggregates.

Raw materials compositions of horasan plasters presented different lime/aggregate ratio values ranging from 1:2 to 3:2 by weight (Figure 4.4, 4.5 and 4.6).

Lime/aggregate ratios of horasan plasters collected from the lower levels were in the range of 1:2-3:2 for the first layers, 4:5-1:1 for the second layers and 4:5-5:4 for the third layers (Figure 4.4, 4.5 and 4.6).

Horasan plasters collected from the upper levels had lime/aggregate ratio values in the range of 2:3-3:2 for the first layers and 1:1-3:2 for the second layers (Figure 4.4, 4.5 and 4.6).

Lime/aggregate ratio values of horasan plasters collected from the domes varied between 2:3 and 1:1 (Figure 4.4, 4.6).

These results revealed that there was not a particular difference between lime/aggregate ratios of upper and lower level horasan plasters.

Lime plasters applied on upper level horasan plasters presented high lime/aggregate ratio values ranging between 17:1 and 99:1 (Figure 4.4, 4.5 and 4.6).

Lime/aggregate ratio values of historic crushed brick/lime mortars ranged between 1:4 and 1:2 (Bakolas 1998, Moropoulou et. al. 2000a, Moropoulou et. al. 2000b, Moropoulou et. el. 2000c, Moropoulou et. al. 2002b). Horasan plasters collected from some Ottoman bath buildings located in Bursa and Edirne and horasan mortars collected from İstanbul city walls had lime/aggregate ratios ranging between 2:3 and 3:1 (Böke et. al. 2004, Şatongar 1998).

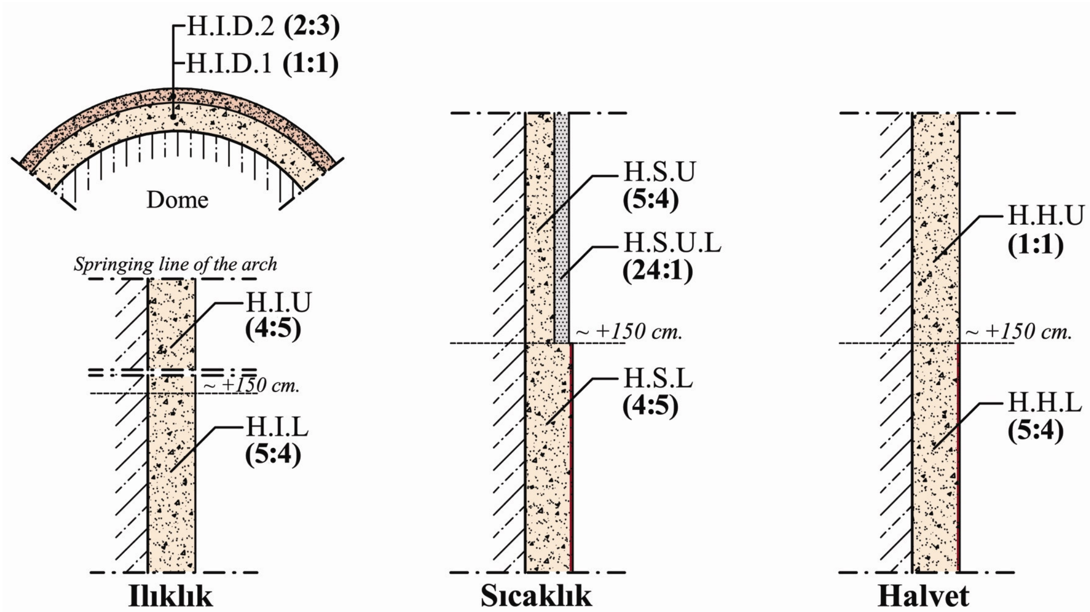


Figure 4.4. Lime/aggregate ratios of plaster samples collected from Hersekzade Bath

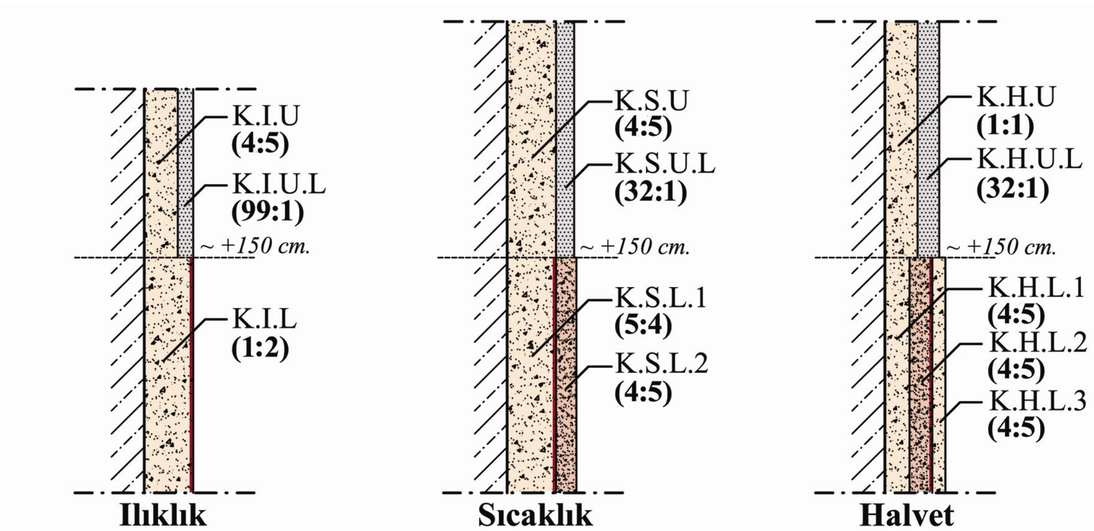


Figure 4.5. Lime/aggregate ratios of plaster samples collected from Kamanlı Bath

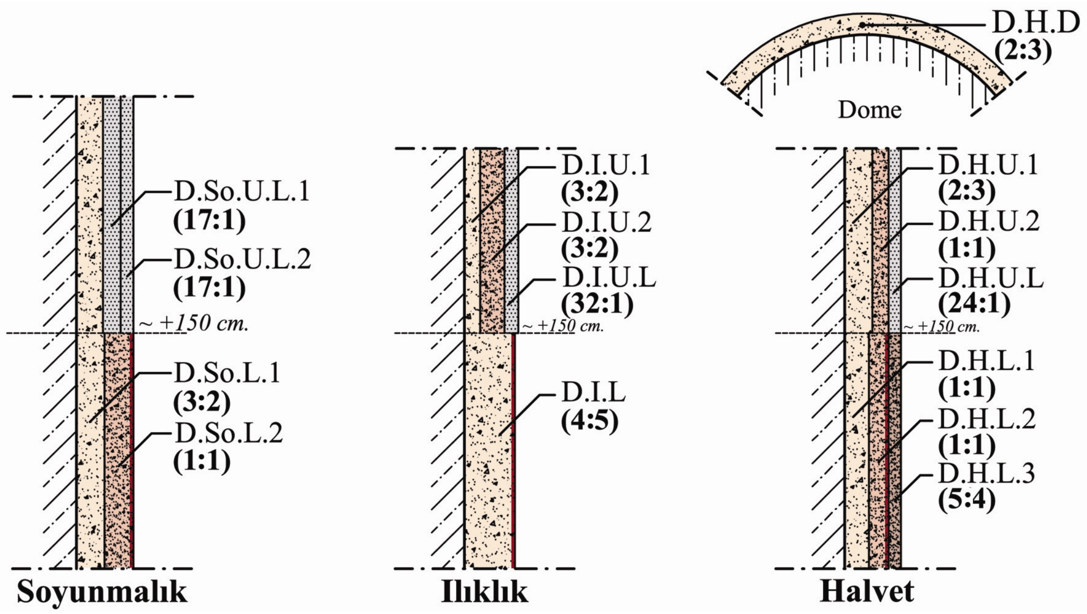


Figure 4.6. Lime/aggregate ratios of plaster samples collected from Düzce Bath

Brick aggregates used in lower level and upper level horasan plasters presented similar particle size distributions with each other (Figure 4.7, 4.8 and 4.9). Aggregates which had particle sizes greater than 1180 µm. constituted the major fraction of total of the aggregates. This major fraction varied in the range of 10-28 % for the lower level horasan plasters and 14-29 % for the upper level horasan plasters. Horasan plaster aggregates collected from the domes which were greater than 1180 µm formed the largest fraction which was between 25-33 %.

The percentage of the aggregates which had particle sizes between 1180-250 µm. ranged between 12 and 28 % for the lower level horasan plasters, 14-27 % for the upper level horasan plasters and 17-26 % for the horasan plasters collected from the domes. Fine aggregates which had particle sizes less than 125µm. constituted the fraction ranging between 8-20 % for the lower level horasan plasters, 7-15 % for the upper level horasan plasters and 6-11 % for the horasan plasters collected from the domes.

Aggregates of lime plasters were composed by fine aggregates with particle sizes less than 125 µm.

All these values were almost in the same ranges with other crushed brick-lime, mortars and plasters used in the Ottoman bath buildings (Böke et. al. 2004).

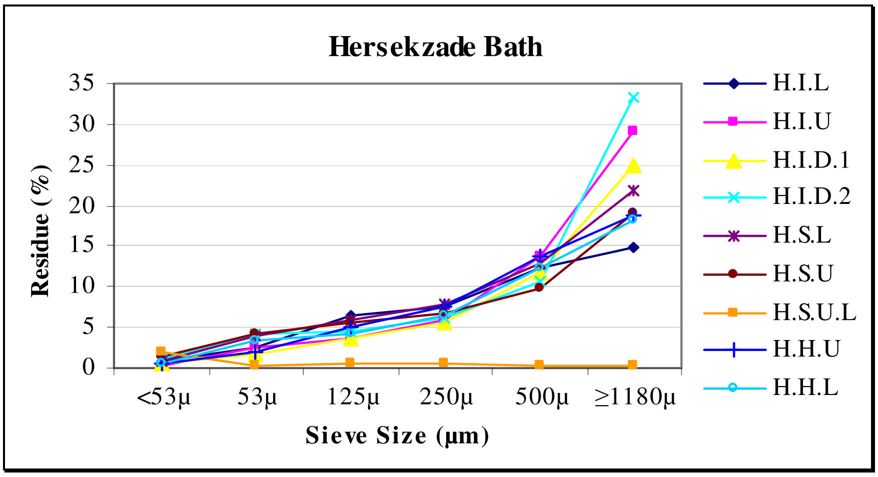


Figure 4.7. Particle size distributions of aggregates used in the plaster samples collected from Hersekzade Bath

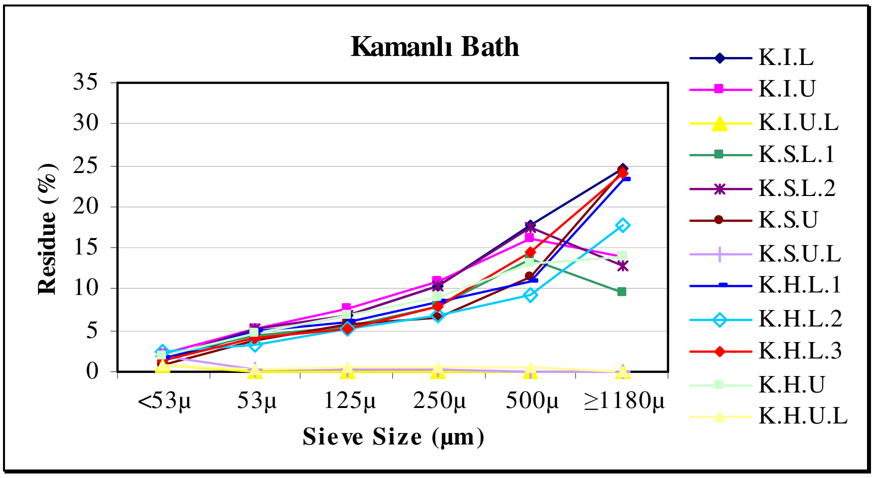


Figure 4.8. Particle size distributions of aggregates used in the plaster samples collected from Kamanlı Bath

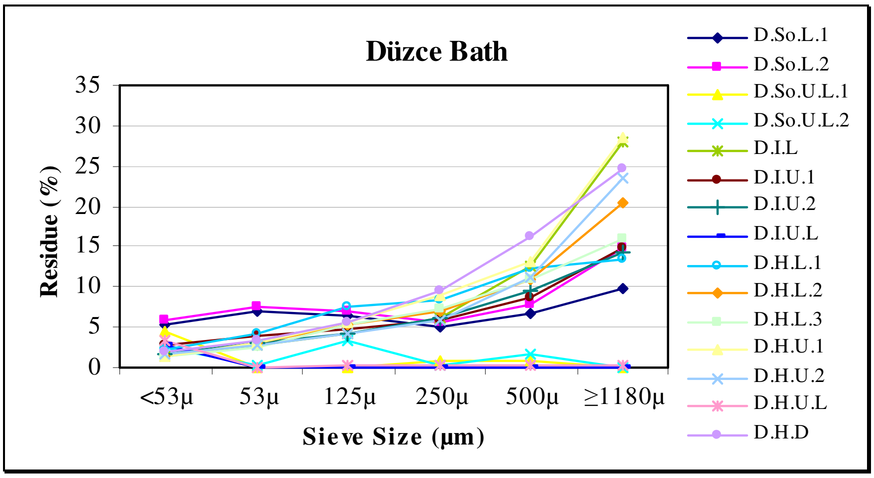


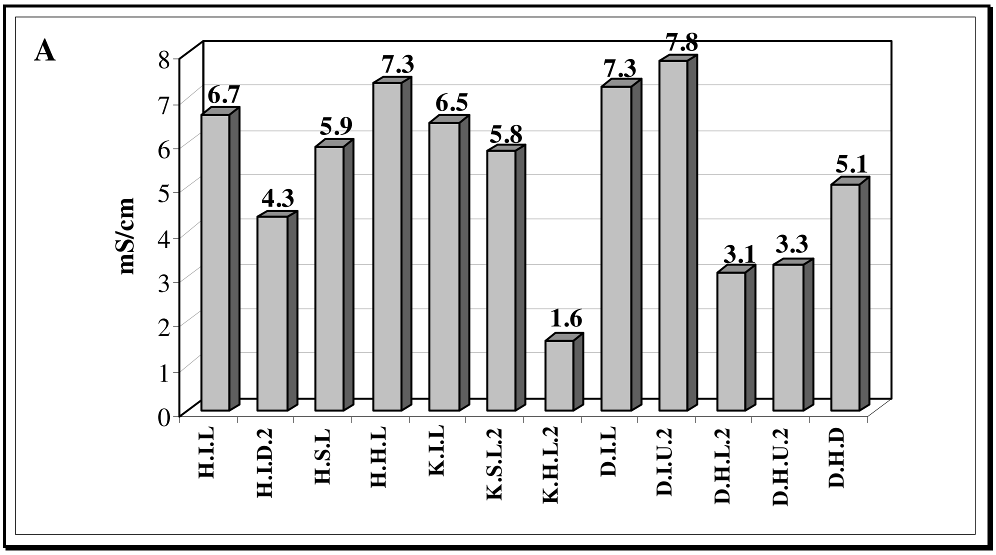
Figure 4.9. Particle size distributions of aggregates used in the plaster samples collected from Düzce Bath

4.3. Pozzolanic Activities of Crushed Brick Aggregates and Building Bricks

In this study, pozzolanic activities of the bricks were found by two different methods. In the first method, the differences in electrical conductivities (mS/cm) were measured before and after addition of powdered bricks (less than 53 micrometer) into saturated calcium hydroxide solution (Luxan et. al. 1989). In the second method, brick powders were added to a saturated solution of calcium hydroxide in order to determine the extent of its reaction with calcium hydroxide. The adsorption of calcium ions by the bricks was determined after 8, 16 and 30 days by measuring the calcium concentration in the calcium hydroxide solution (Liebig et. al. 1998).

In the first method, the difference between the electrical conductivity values over 1.2 mS/cm revealed good pozzolanicity while the values between 0.4-1.2 mS/cm indicated variable pozzolanicity of the material, and values less than 0.4 mS/cm indicated that the material is non-pozzolanic (Luxan et. al. 1989).

Electrical conductivity measurements showed that all examined crushed bricks used as aggregates had good pozzolanicity with values ranging between 1.6-7.8 mS/cm (Figure 4.10). However, the pozzolanicity values of building bricks were between 0.2-0.7 mS/cm that they can be considered as non-pozzolanic (Figure 4.11).



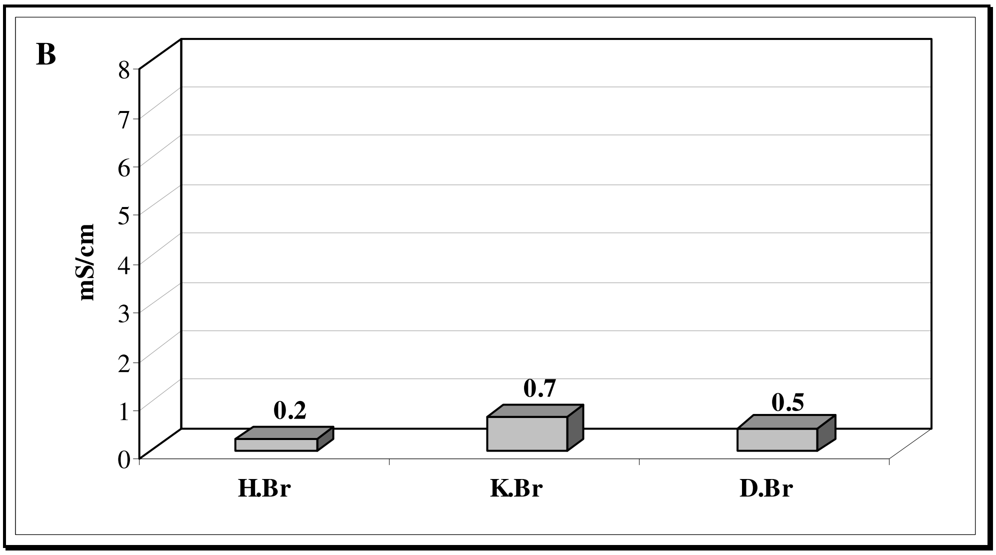
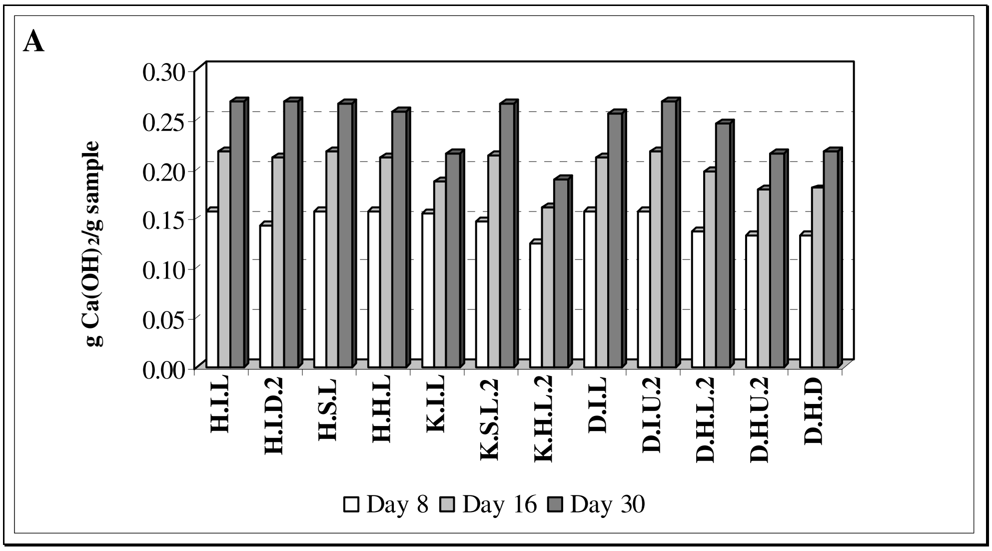


Figure 4.10. Pozzolanic activity values of brick aggregates (A) and building bricks (B) by electrical conductivity measurement method

Similar results were obtained from the second method with electrical conductivity measurements. Brick aggregates of the horasan plasters reacted with calcium hydroxide more than those of the building bricks (Figure 4.11). At the end of 30 days, amount of adsorbed calcium hydroxide ($Ca(OH)_2$) by aggregates varied between 0.19 and 0.27 g. However, it was about 0.15 g. for building bricks. Similar results have been obtained by Böke et al. (Böke et. el. 2004).

Amount of releasing sodium oxide (Na_2O) were in the range of 6.5-23.4 mg. for brick aggregates. It was found about 22 mg. for building bricks (Figure 4.12). The similar results were also obtained in the analysis of potassium ions (Figure 4.13).

The results indicated that amounts of releasing sodium oxide (Na_2O) and potassium oxide (K_2O) were higher in the non-pozzolanic bricks. It may explained by the high amounts of feldspar minerals in the composition of non-pozzolanic bricks (Table 4.1, 4.2, 4.3).



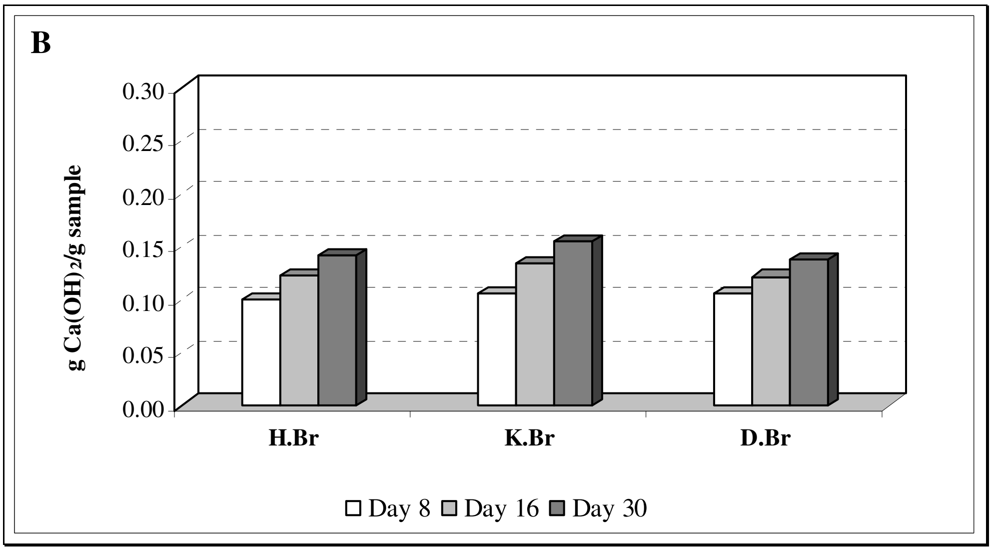


Figure 4.11. Amount of lime reacted with brick aggregate (A) and building brick (B) powders after 8, 16 and 30 days

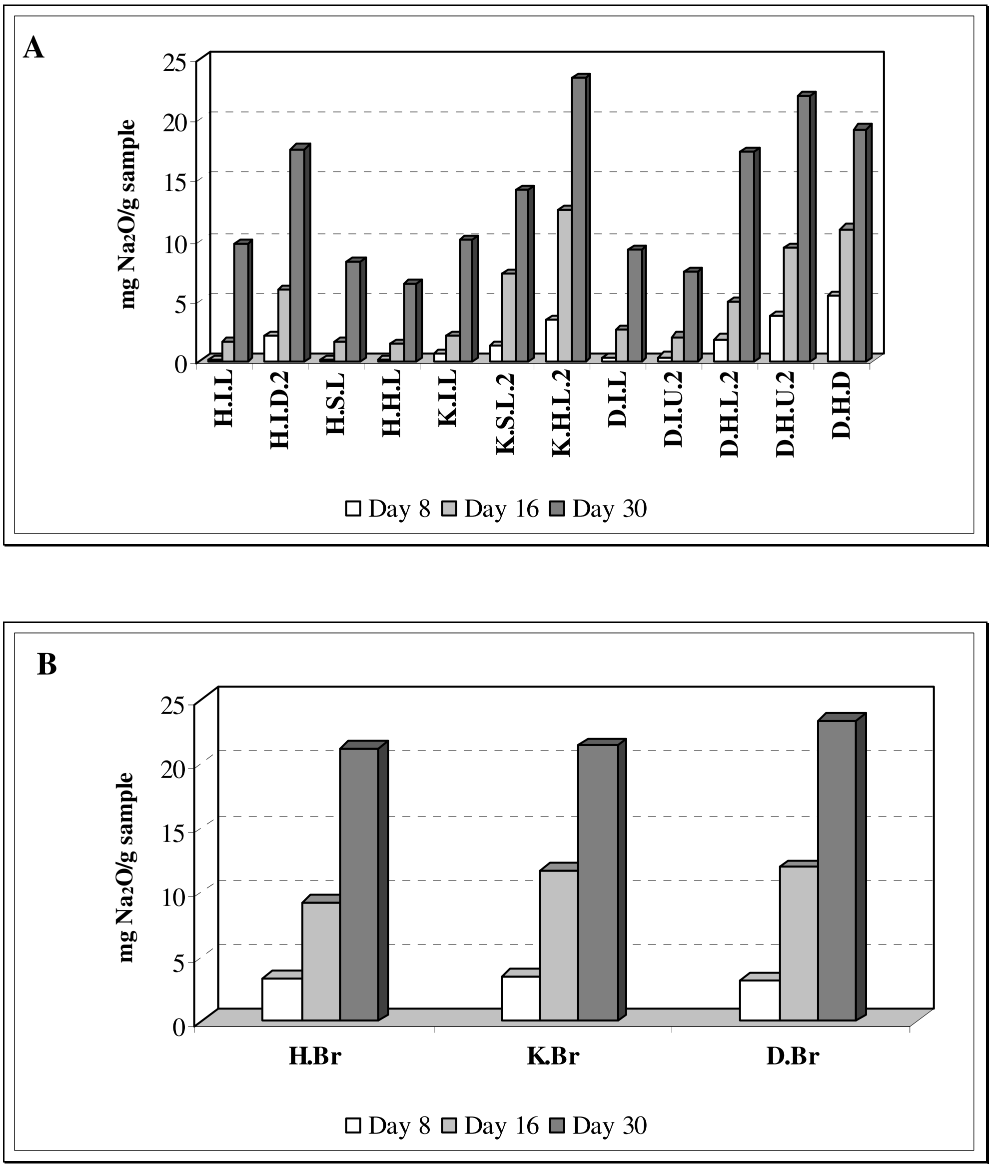


Figure 4.12. The amount of sodium oxide (Na_2O) released by brick aggregate (A) and building brick (B) powders after 8, 16 and 30 days

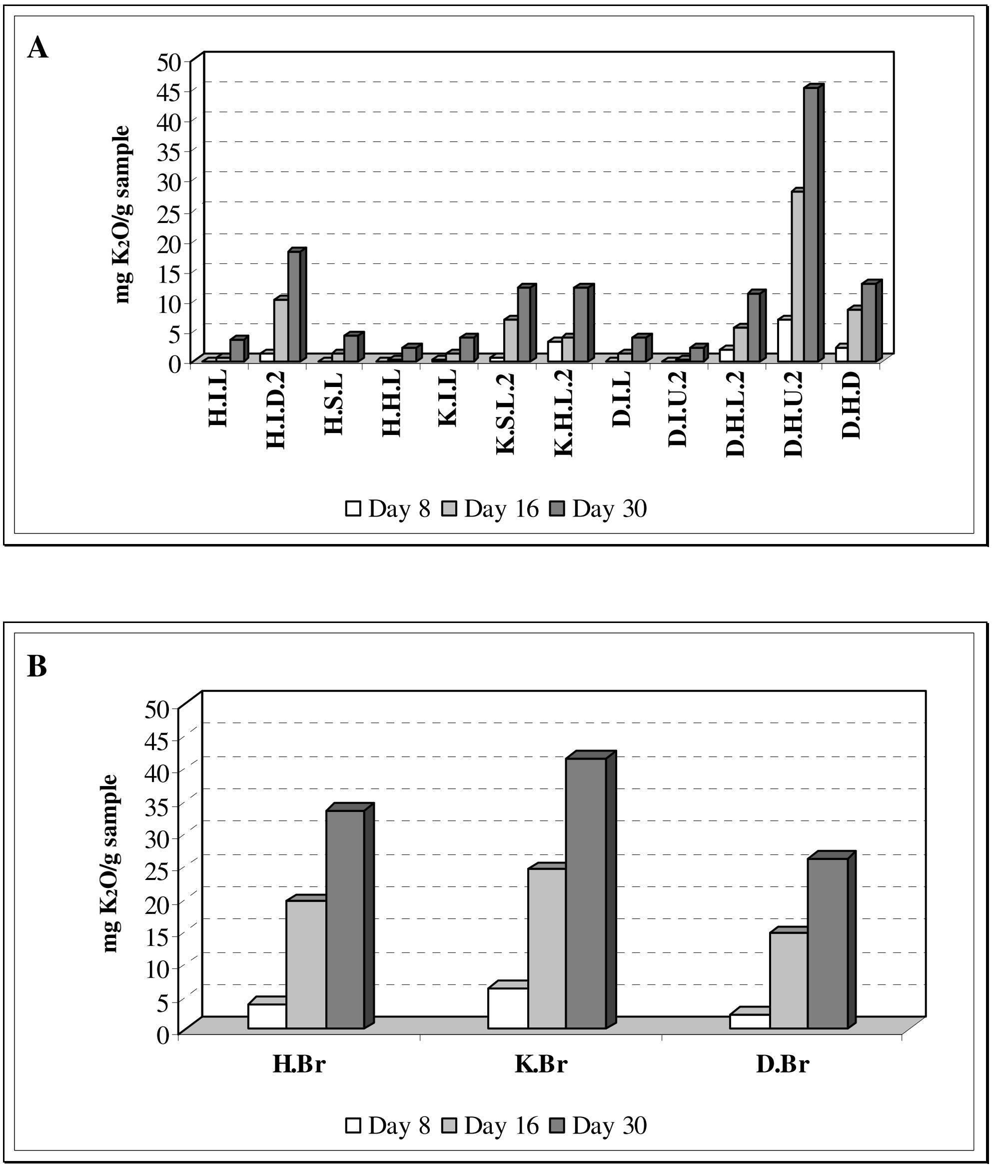
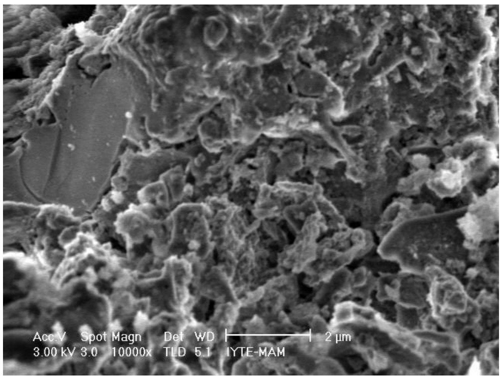


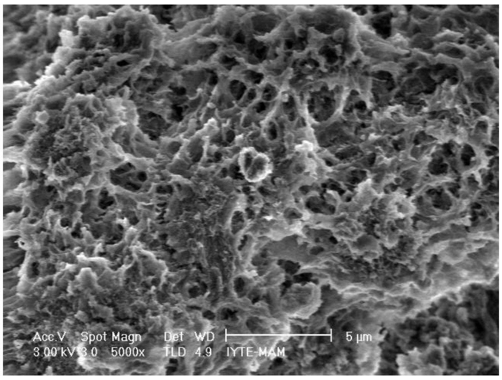
Figure 4.13. The amount of potassium oxide (K_2O) released by brick aggregate (A) and building brick powders (B) after of 8, 16 and 30 days

Microstructural properties and chemical composition of the brick aggregates which had kept in saturated calcium hydroxide solution for 30 days were determined by SEM-EDS analysis.

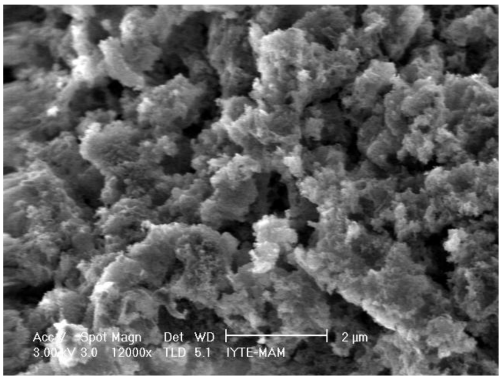
Before Reaction | **After Reaction**



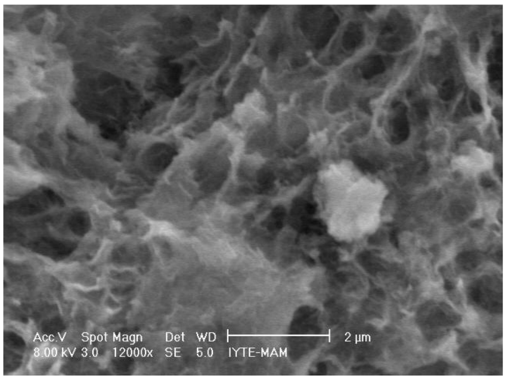
(TLD-10000X)



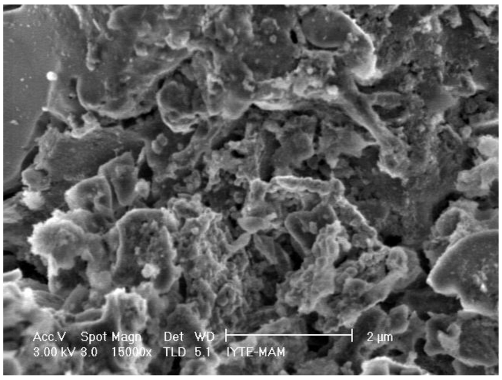
(TLD-5000X)



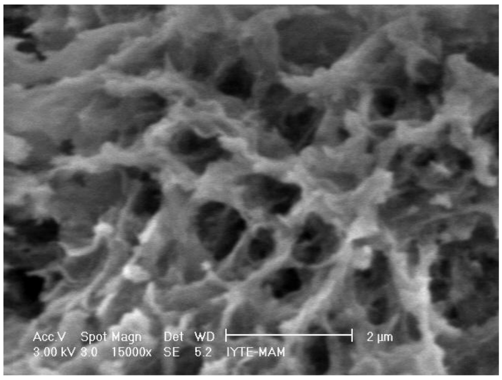
(TLD-12000X)



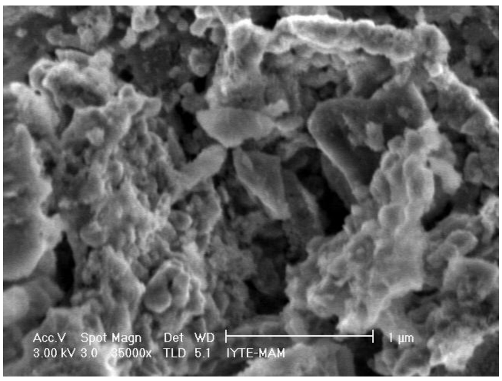
(SE-12000X)



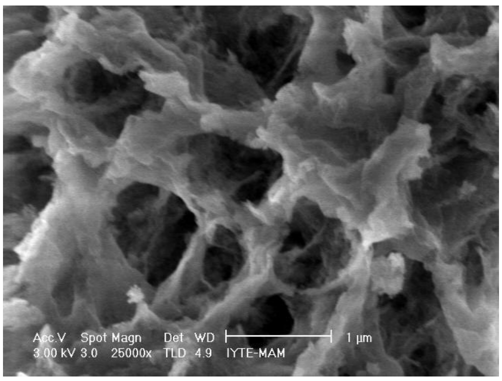
(TLD-15000X)



(SE-15000X)



(TLD-35000X)



(TLD-25000X)

Figure 4.14. TLD (through lens detector) and SE (secondary electron) images of brick aggregates before and after reaction with lime for 30 days

Before reaction of brick powders with lime, amorphous structures were observed in SEM images (Figure 4.14). After reaction, gel like structures were observed in SEM images. Calcium peaks were not observed in the SEM-EDS spectrum of the brick aggregates before their reaction with lime (Figure 4.15). But after 30 days, Ca was observed (Figure 4.15). This might indicate the formation of calcium silicate hydrate (CSH). However, the expected main peaks of calcium silicate hydrate and calcium aluminate hydrate formations were not observed in XRD spectrum. This could be explained by the amorphous character of the hydraulic products (Haga et. al. 2002).

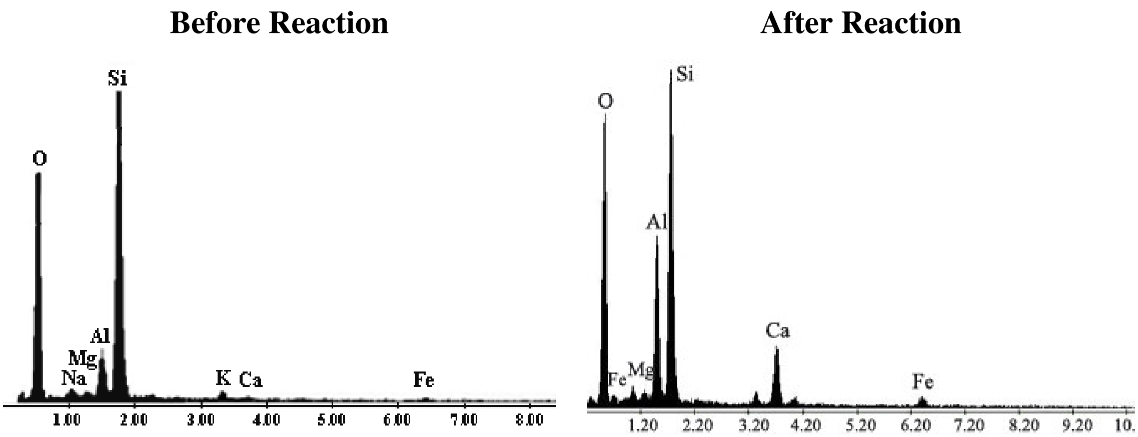


Figure 4.15. EDS spectrum of brick powders before and after reaction with lime for 30 days (H.I.D.2)

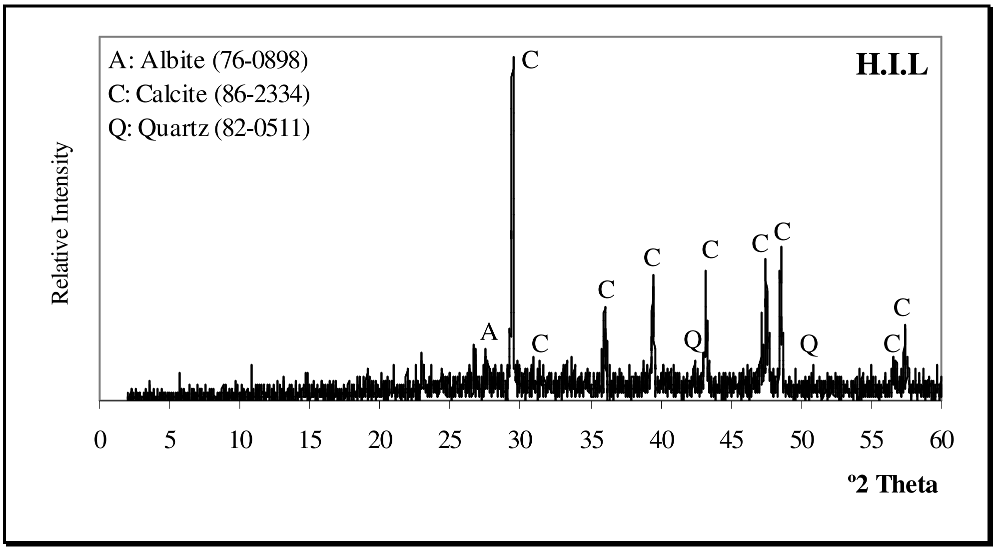
4.4. Mineralogical Compositions of Plasters, Crushed Brick Aggregates and Building Bricks

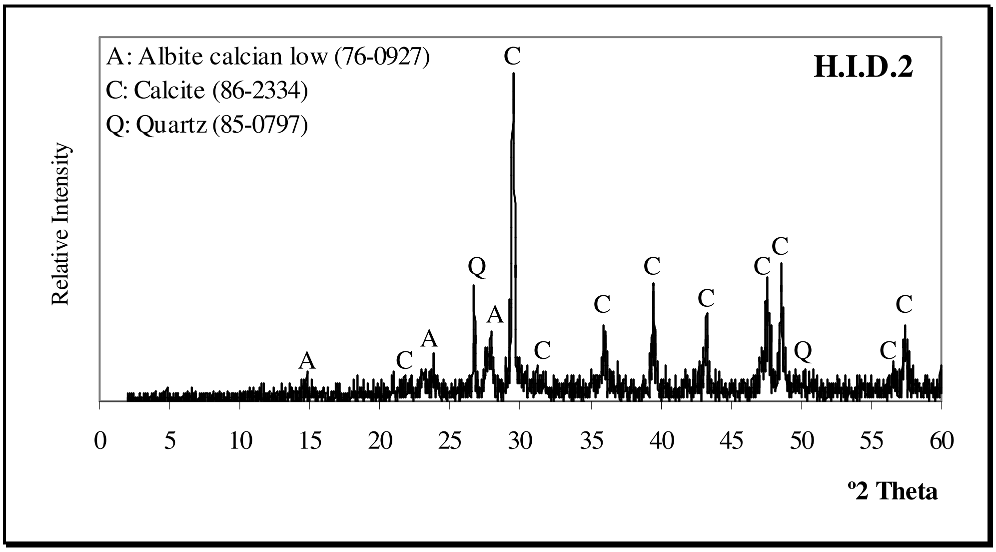
Mineralogical compositions of plasters, crushed brick aggregates and building bricks were determined by using an X-ray Diffractometer (XRD). The determined minerals were shown in the XRD diffraction patterns with their first letters.

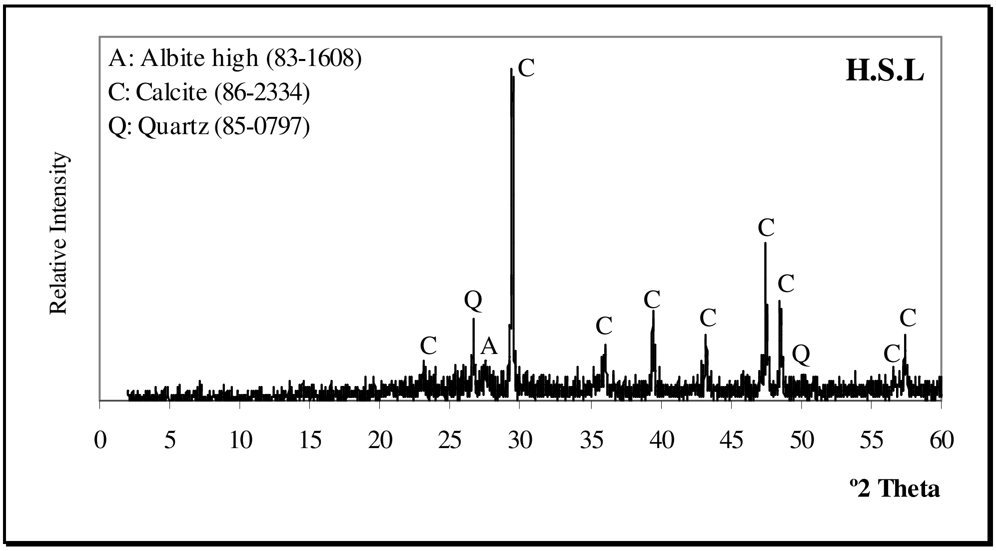
4.4.1. Mineralogical Compositions of Plasters

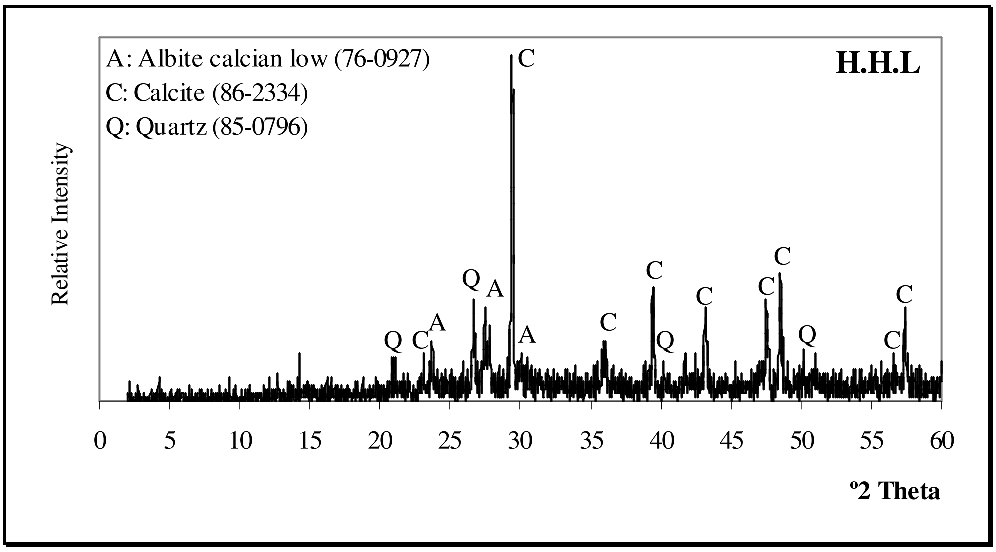
XRD patterns of the horasan plaster matrices showed that they were mainly composed of calcite (C: $CaCO_3$), quartz (Q: SiO_2) and albite (A: ($Na(AlSi_3O_8)$))(Figure 4.16). Calcite was derived from carbonated lime, and quartz and albite were derived from brick powders. The expected main XRD peaks of calcium silicate hydrate and calcium aluminate hydrate formations were not observed in the plasters matrices. This might be due to amorphous characters of these hydraulic products (Haga et. al. 2002).

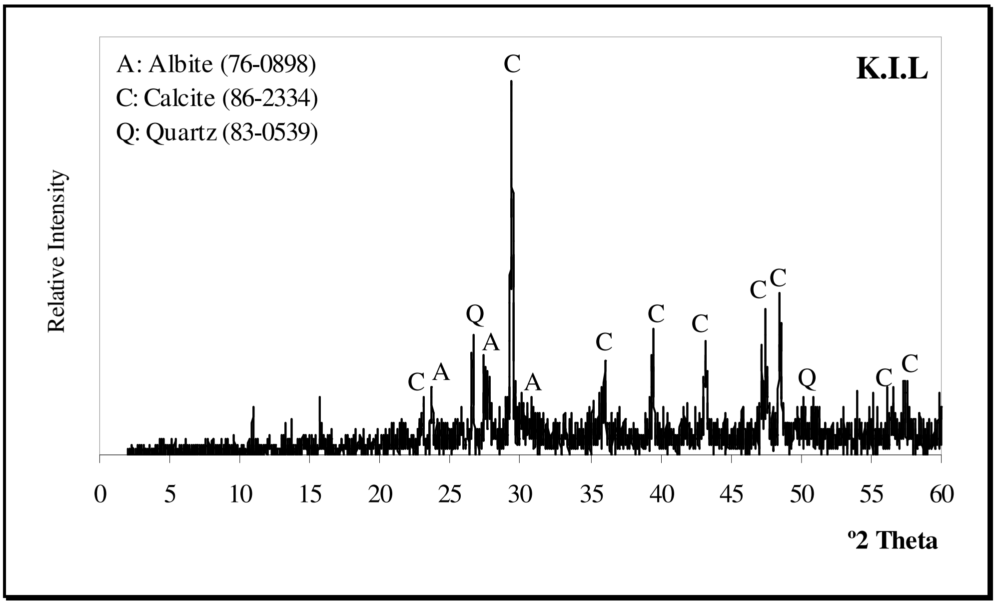
The similar results were indicated for other crushed brick-lime, mortars and plasters collected from several historic buildings (Moropoulou et. al. 1995, Böke et. al. 2004).

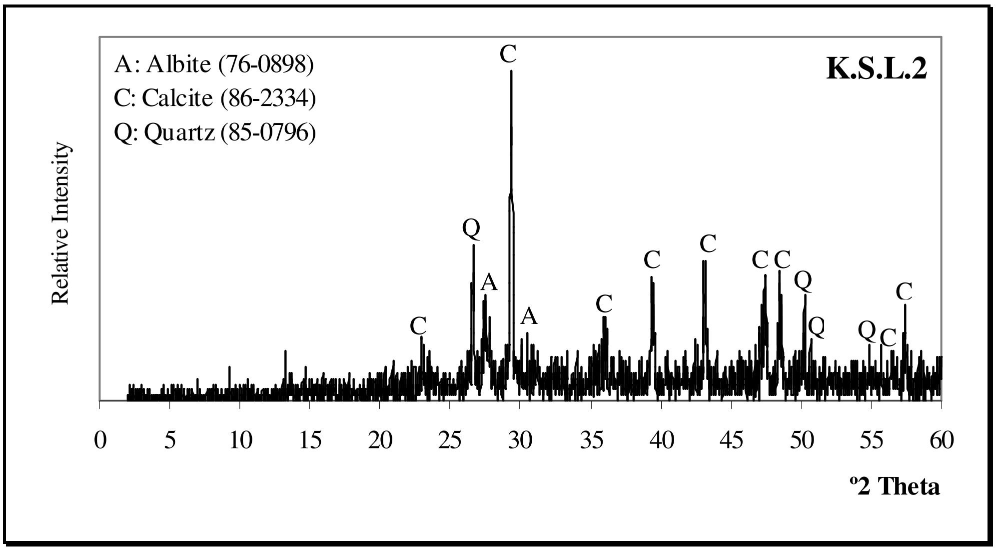


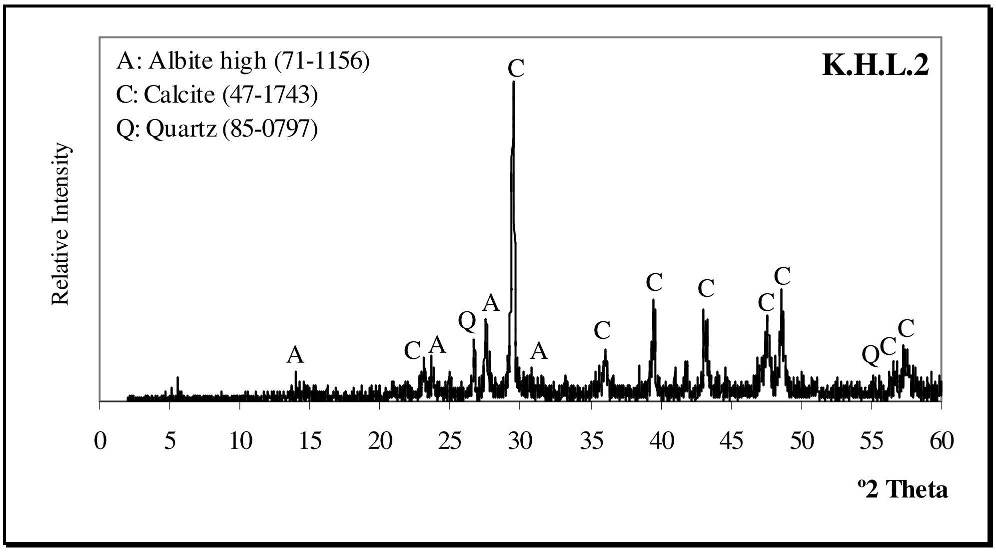


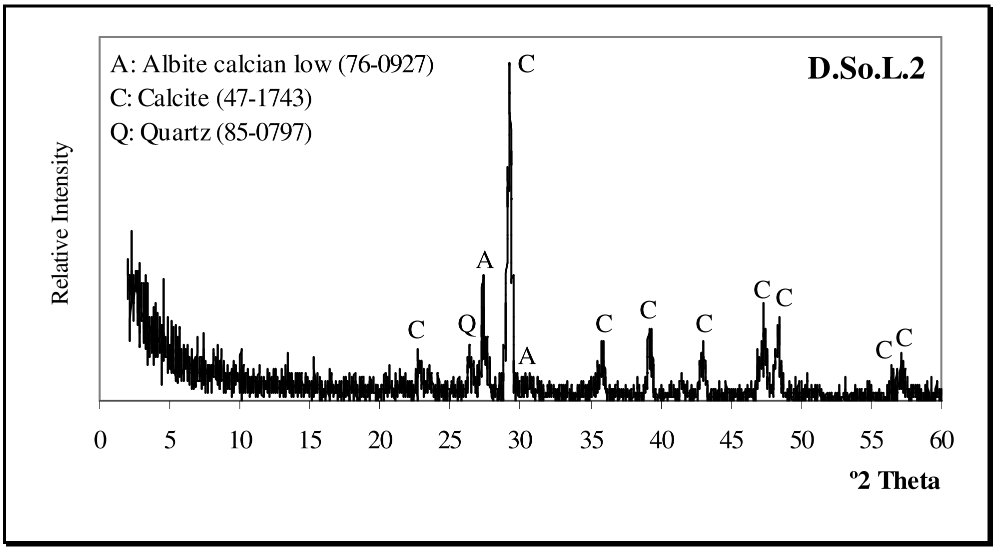

A: Albite high (83-1608)
C: Calcite (86-2334)
Q: Quartz (85-0797)
H.S.L
Relative Intensity
°2 Theta

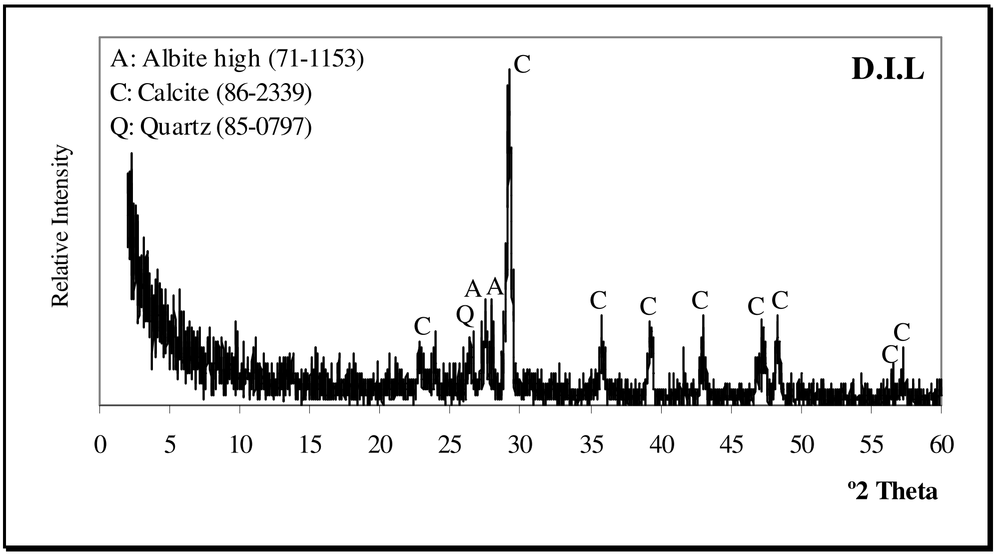

A: Albite calcian low (76-0927)
C: Calcite (86-2334)
Q: Quartz (85-0796)
H.H.L
Relative Intensity
°2 Theta

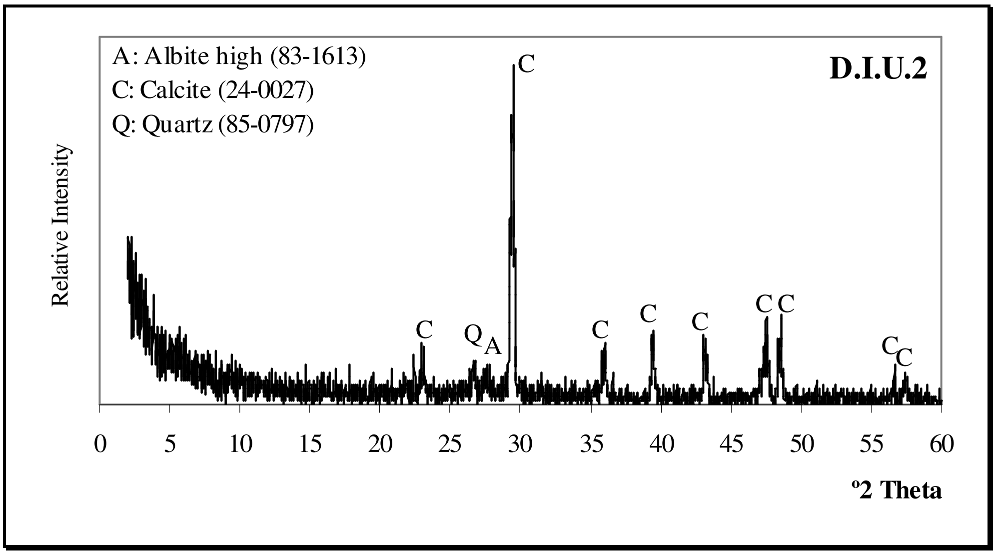

A: Albite (76-0898)
C: Calcite (86-2334)
Q: Quartz (83-0539)
K.I.L
Relative Intensity
°2 Theta

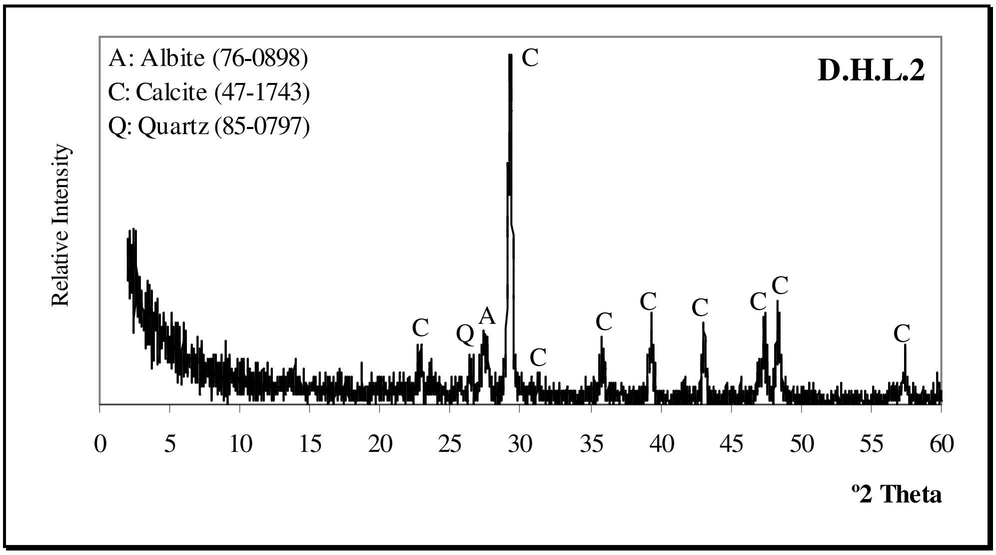

A: Albite (76-0898)
C: Calcite (86-2334)
Q: Quartz (85-0796)
K.S.L.2
Relative Intensity
°2 Theta

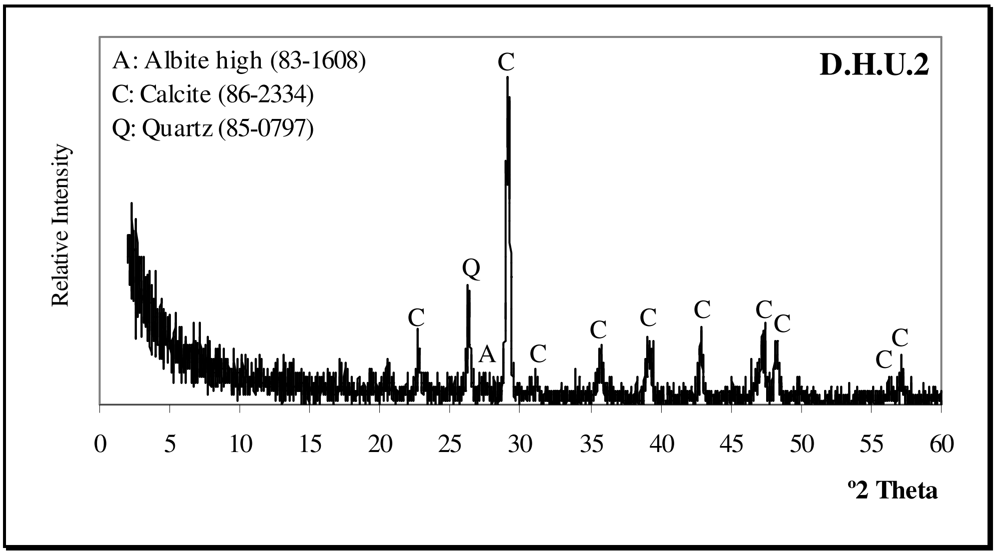

A: Albite high (71-1156)
C: Calcite (47-1743)
Q: Quartz (85-0797)
K.H.L.2
Relative Intensity
°2 Theta


A: Albite calcian low (76-0927)
C: Calcite (47-1743)
Q: Quartz (85-0797)
D.So.L.2
Relative Intensity
°2 Theta


A: Albite high (71-1153)
C: Calcite (86-2339)
Q: Quartz (85-0797)
D.I.L
Relative Intensity
°2 Theta


A: Albite high (83-1613)
C: Calcite (24-0027)
Q: Quartz (85-0797)
D.I.U.2
Relative Intensity
°2 Theta


A: Albite (76-0898)
C: Calcite (47-1743)
Q: Quartz (85-0797)
D.H.L.2
Relative Intensity
°2 Theta



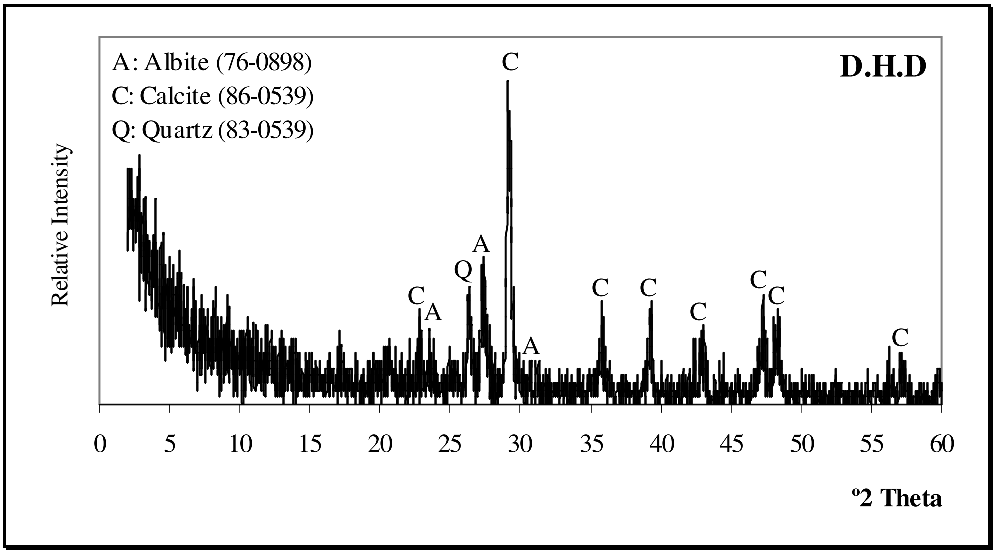
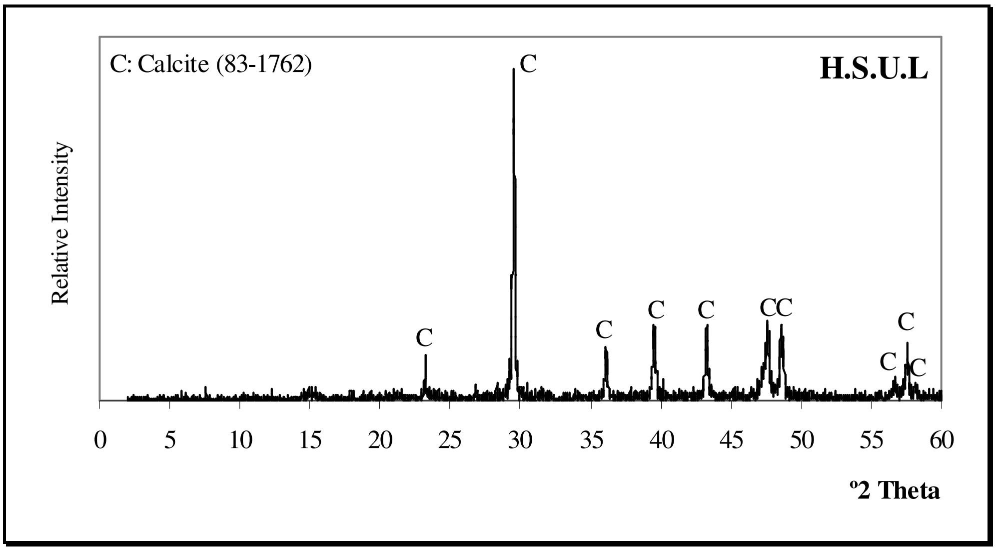
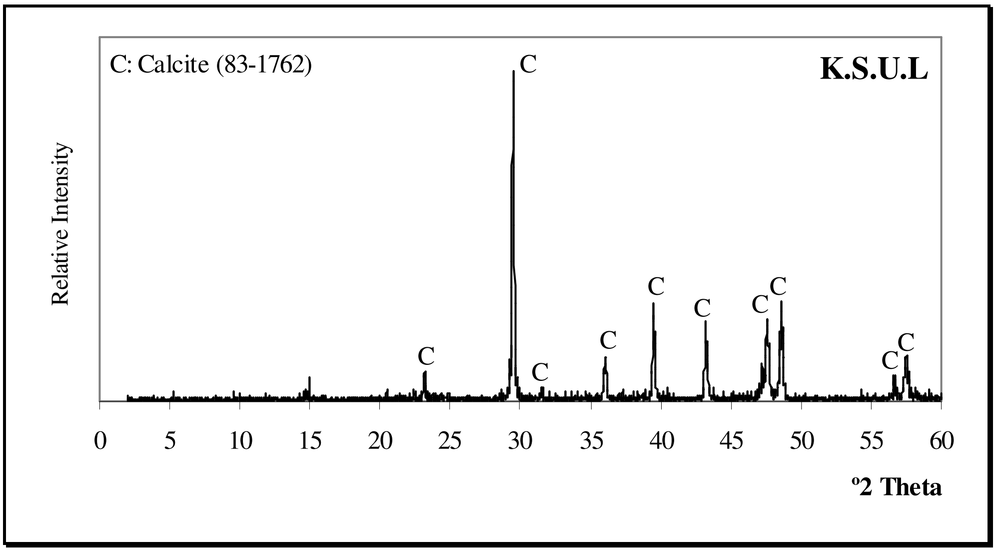
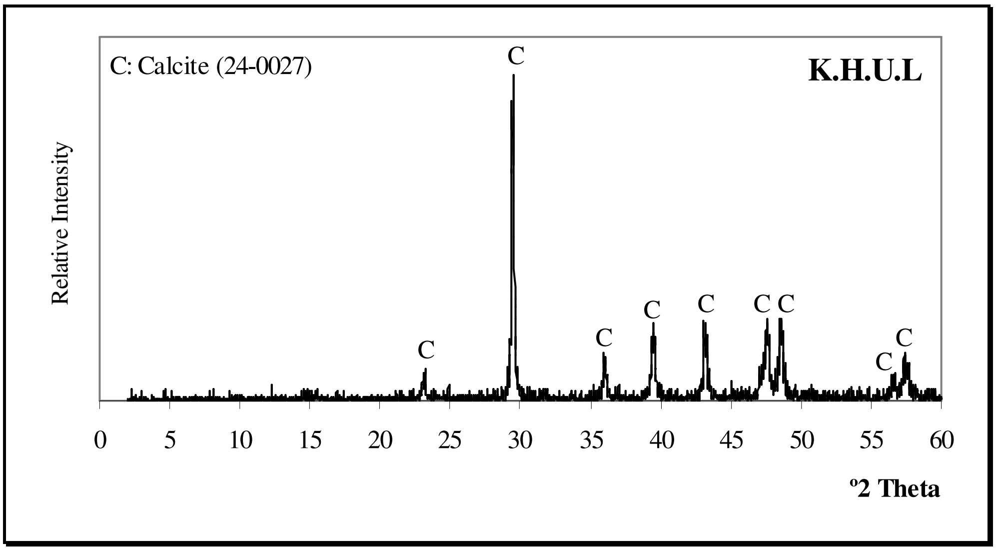


Figure 4.16. XRD patterns of some horasan plaster samples

Mineralogical compositions of the lime plasters were also determined by XRD. Only strong calcite (C) peaks were observed in their XRD patterns. These results showed that lime used in manufacturing of the plasters was almost pure (Figure 4.17).


C: Calcite (83-1762)
H.S.U.L
Relative Intensity
C
0 5 10 15 20 25 30 35 40 45 50 55 60
°2 Theta


C: Calcite (83-1762)
K.S.U.L
Relative Intensity
C
0 5 10 15 20 25 30 35 40 45 50 55 60
°2 Theta


C: Calcite (24-0027)
K.H.U.L
Relative Intensity
C
0 5 10 15 20 25 30 35 40 45 50 55 60
°2 Theta

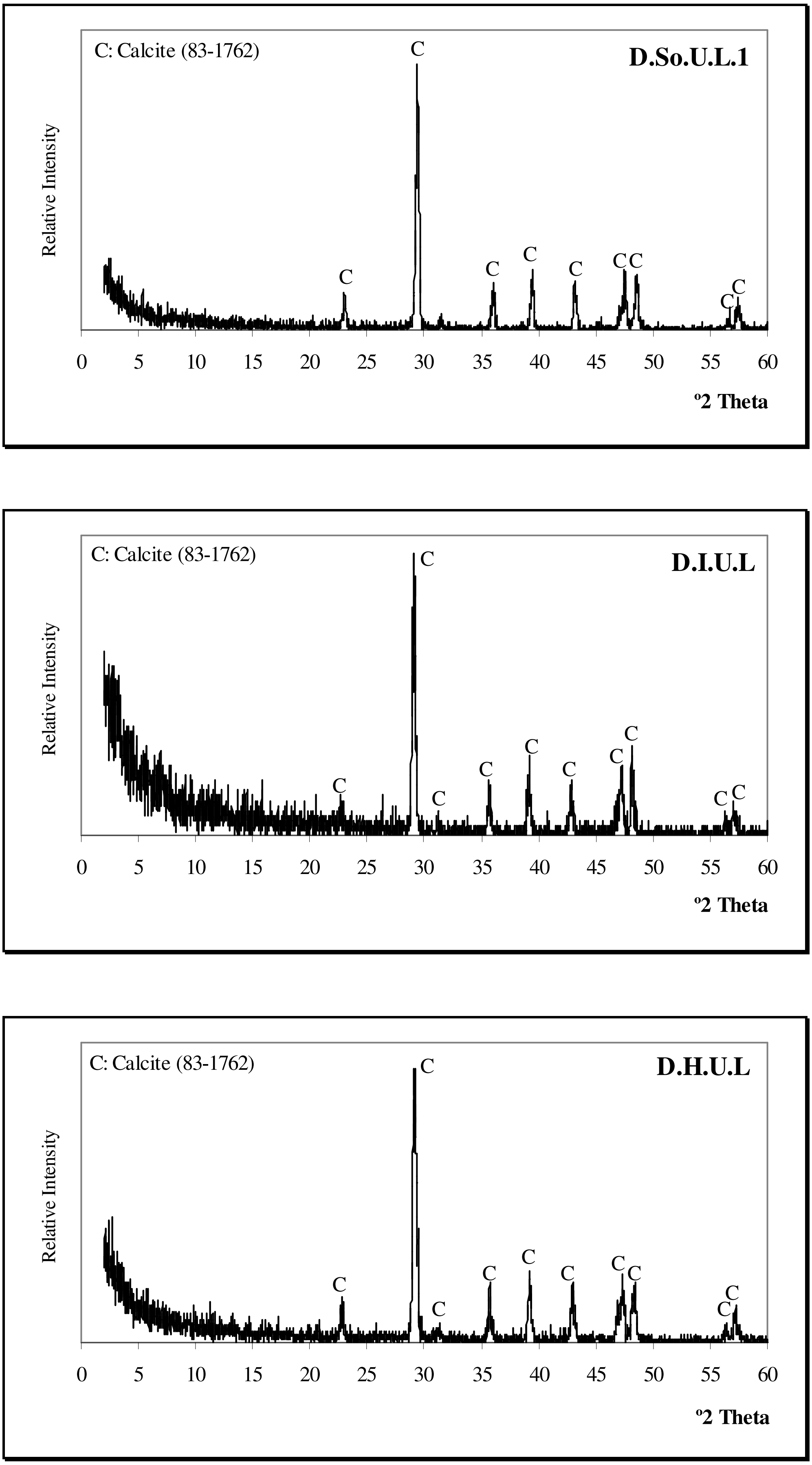


Figure 4.17. XRD patterns of some lime plaster samples

4.4.2. Mineralogical Compositions of Crushed Brick Aggregates and Building Bricks

In XRD patterns of crushed brick aggregates and building brick samples, quartz (Q: SiO_2), albite (A: ($Na(AlSi_3O_8)$)) and potassium feldspar (F: $KAl_2Si_2O_5(OH)_4$) minerals were mainly observed (Figure 4.18, 4.19).

Besides the determination of their mineralogical compositions, XRD patterns gave information about their firing temperatures and pozzolanic activities. If the bricks were manufactured by using Ca-rich clays, the presence of gehlenite (800 ºC), diopside (850 ºC), wollastonite (900-1050 ºC) minerals in their XRD patterns indicate high firing temperature (Reaction I- IV) (Cardiano et. al. 2004).

If Ca-poor clays used, the presence of hematite indicates a firing temperature of 850 ºC (Cardiano et. al. 2004).

"$KAl_4(Si_7Al)O_{20}(OH)_4 + 4\ CaCO_3 \rightarrow KAlSi_3O_8 + 2Ca_2Al_2SiO_7 + 2SiO_2 + 4CO_2 + 2\ H_2O$"
Illite Calcite KFeldspar Gehlenite ***(I)***

"$KAl_4(Si_7Al)O_{20}(OH)_4 + 5\ CaCO_3 \rightarrow 5\ CaAl_2Si_2O_8 + 4\ SiO_2 + 5\ CO_2 + K_2O + 4\ H_2O$"
Illite Calcite Anorthite ***(II)***

"$CaMg(CO_3)_2 + 2\ SiO_2 \rightarrow CaMgSi_2O_6 + 2\ CO_2$"
Dolomite Diopside ***(III)***

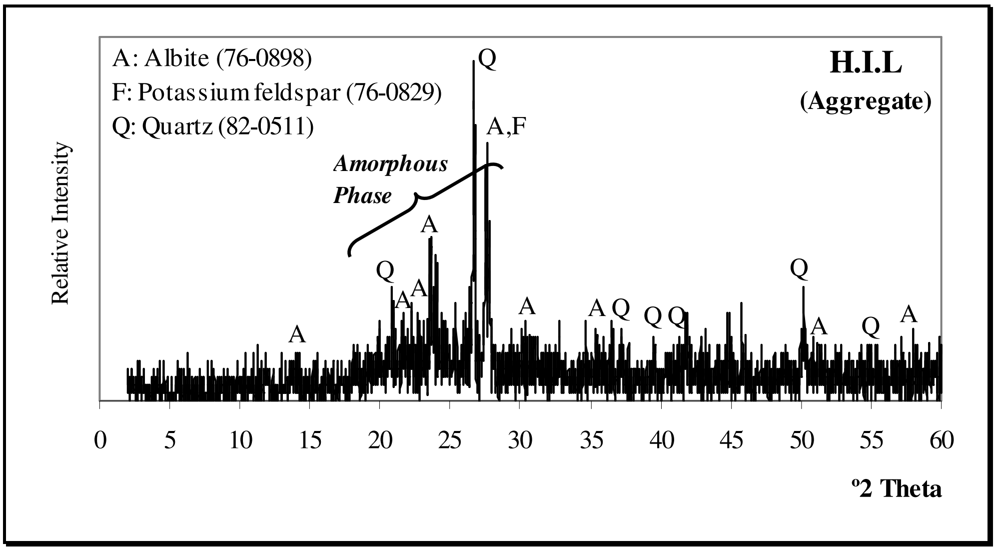
"$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$"
Calcite Wollastonite ***(IV)***

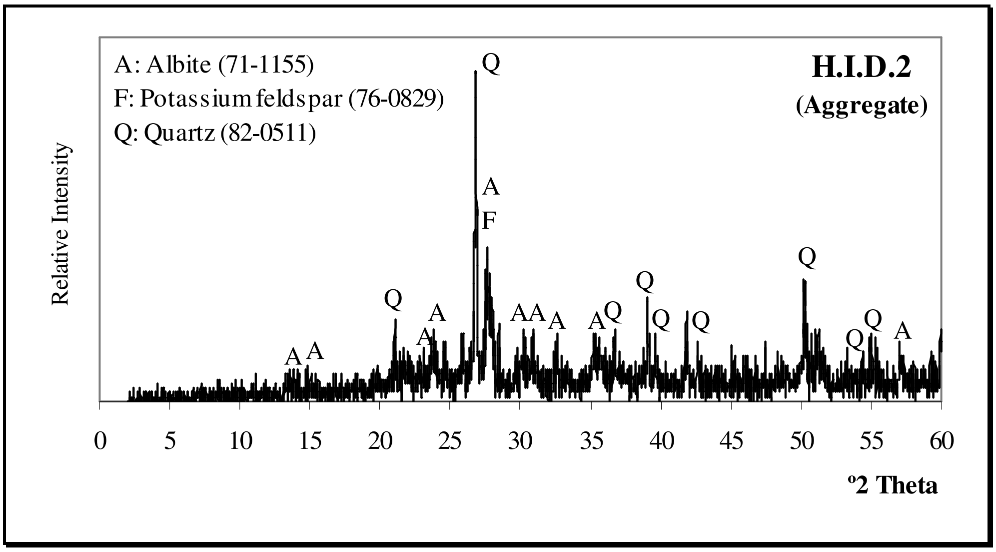
In the XRD patterns of brick aggregates and building bricks, high firing temperature minerals were not observed. This revealed that all bricks were heated at temperatures below 850 ºC.

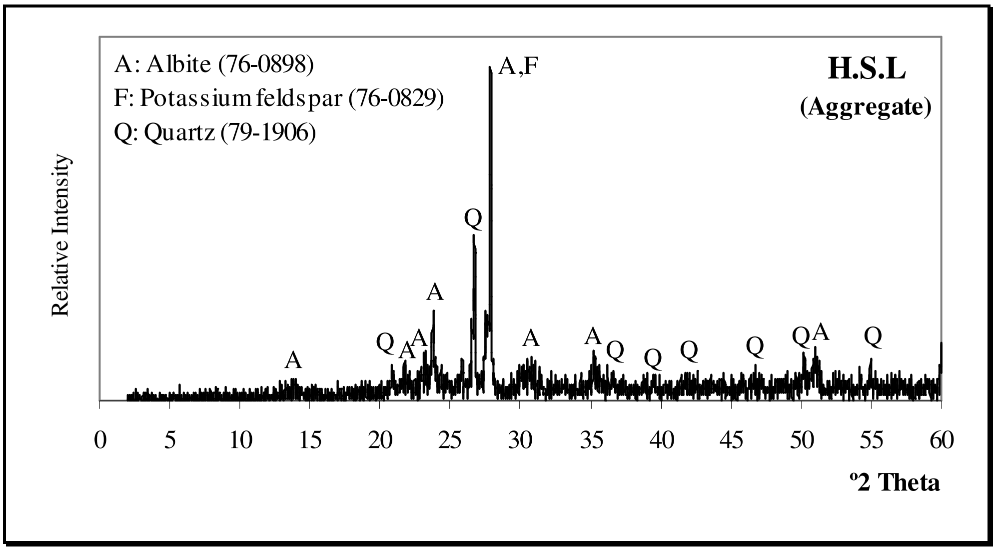
XRD analyses also gave information about the pozzolanicity of bricks. The diffuse band between 20-30 degrees 2θ showed the presence of pozzolanic amorphous substances probably derived from the high amounts of heated clay minerals (Sujeong et. al. 1999).

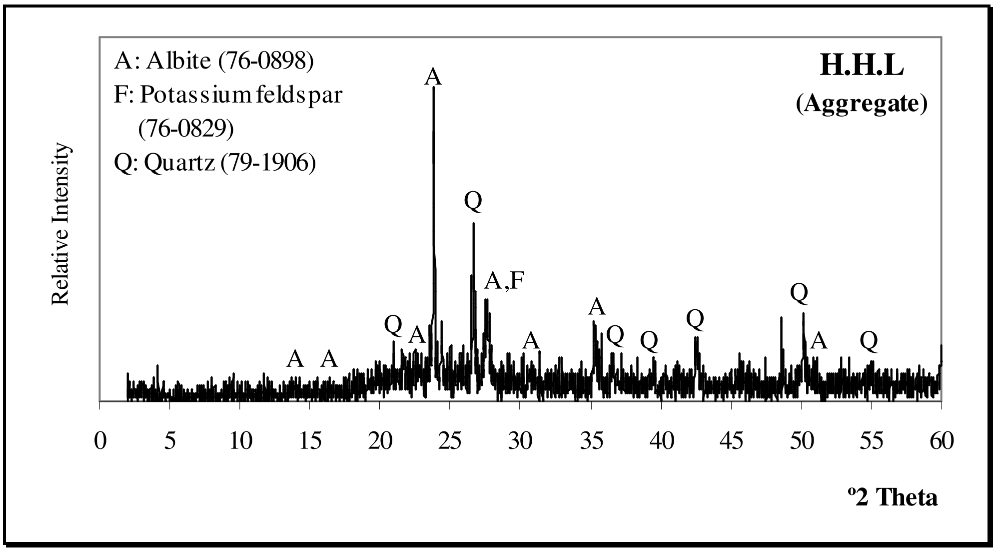
In the XRD patterns of brick aggregates of horasan plasters, the diffuse band between 20-30 degrees 2θ was observed (Figure 4.18). This might indicate the use of high amounts of clay minerals in their manufacturing. However, the diffuse band was not observed in the XRD patterns of the bricks used in the domes as construction materials (Figure 4.19). This might show the use of low amount of clay minerals in their preparation.

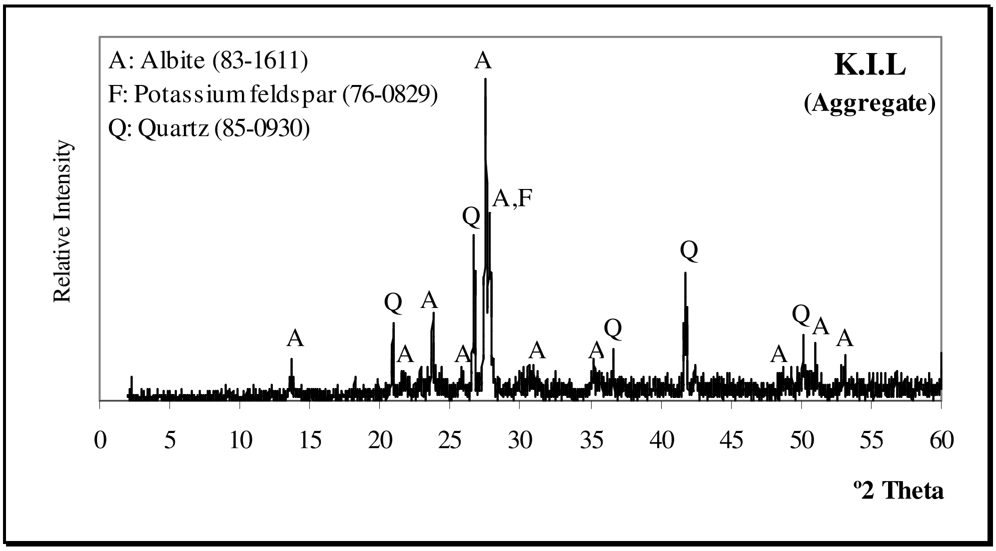
The pozzolanic activity measurement confirmed also the presence of higher amounts of amorphous substances in the composition of the brick aggregates than those of the building bricks.

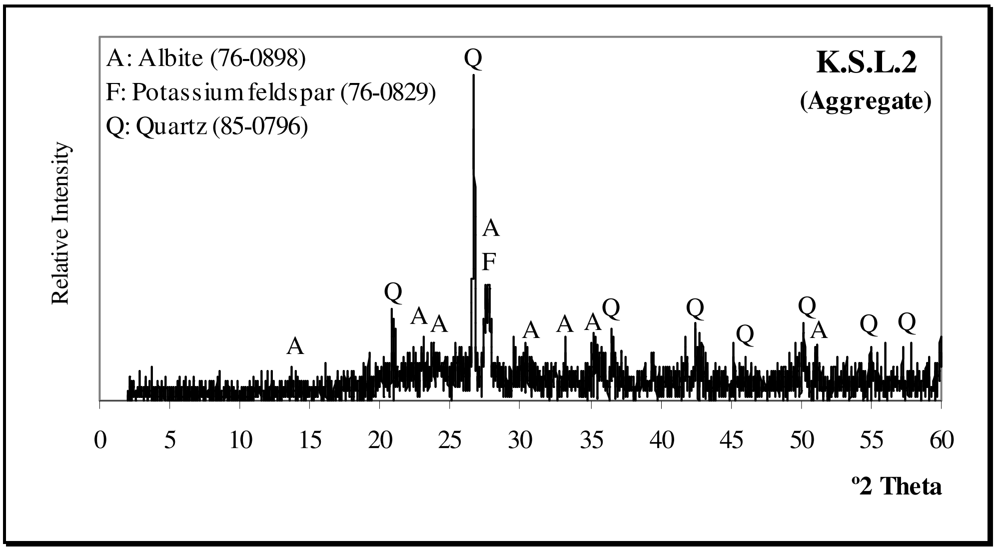


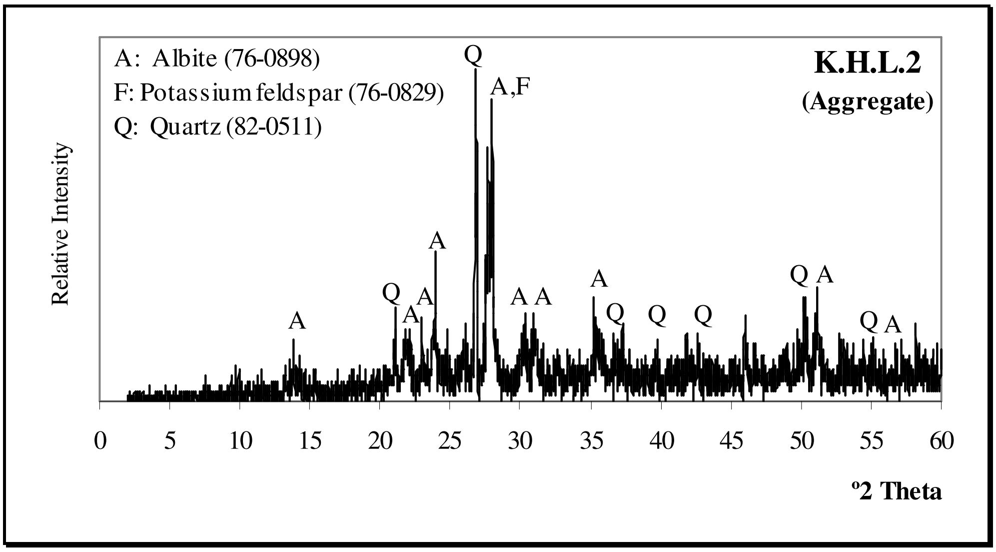


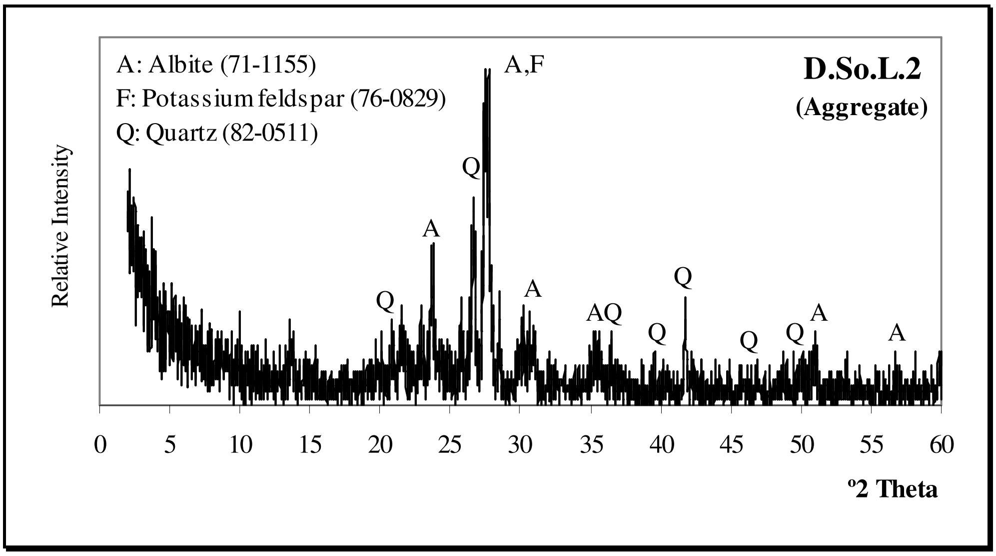

A: Albite (76-0898)
F: Potassium feldspar (76-0829)
Q: Quartz (79-1906)
H.S.L
(Aggregate)
Relative Intensity
°2 Theta

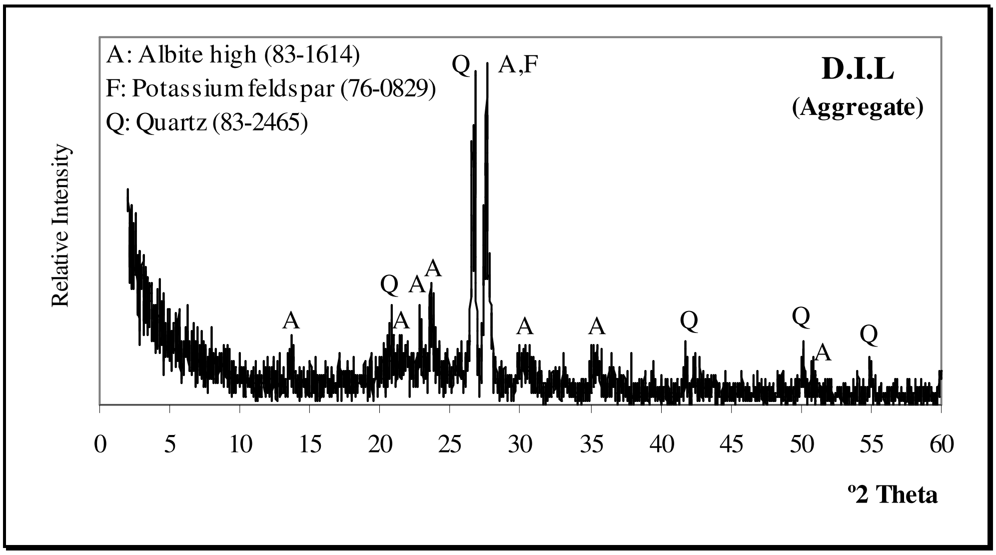

A: Albite (76-0898)
F: Potassium feldspar (76-0829)
Q: Quartz (79-1906)
H.H.L
(Aggregate)
Relative Intensity
°2 Theta

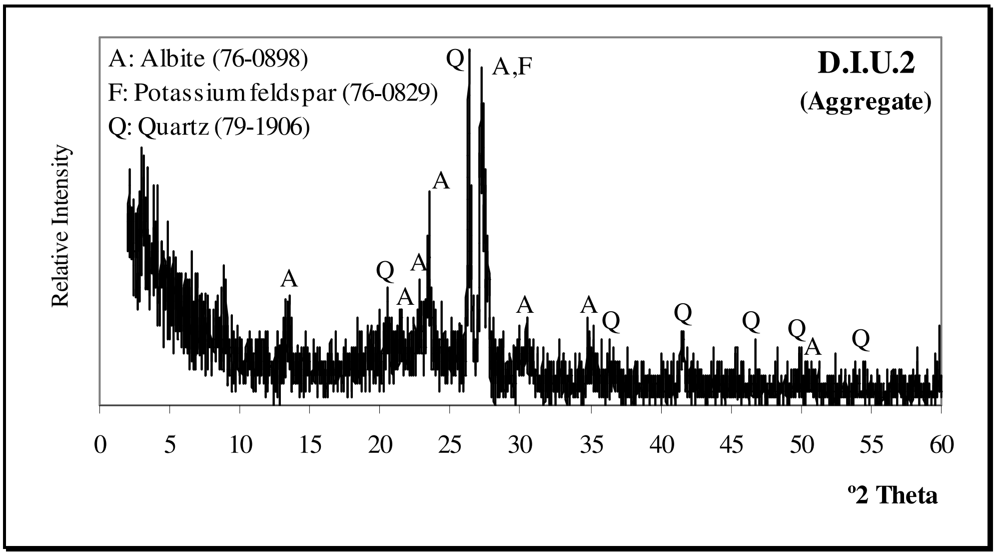

A: Albite (83-1611)
F: Potassium feldspar (76-0829)
Q: Quartz (85-0930)
K.I.L
(Aggregate)
Relative Intensity
°2 Theta

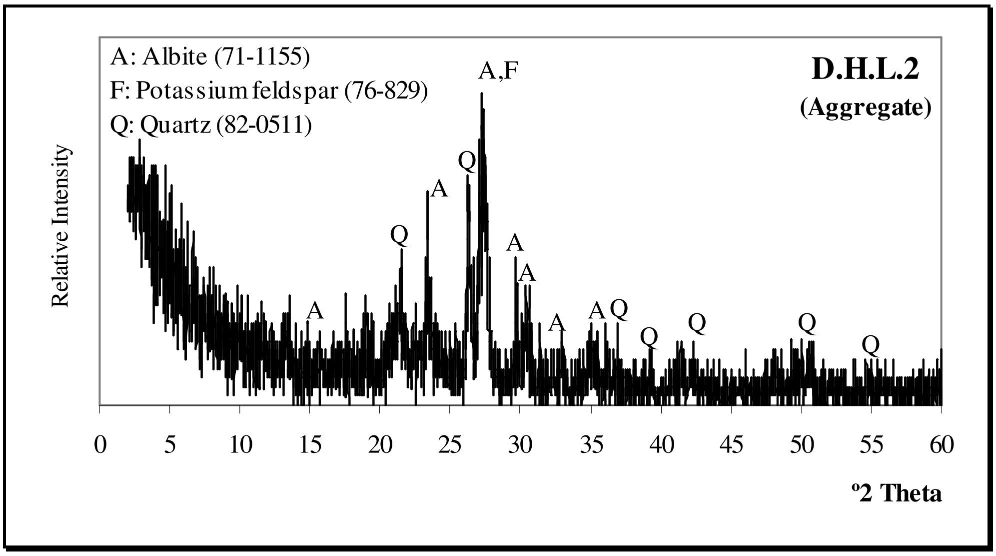

A: Albite (76-0898)
F: Potassium feldspar (76-0829)
Q: Quartz (85-0796)
K.S.L.2
(Aggregate)
Relative Intensity
°2 Theta
0 5 10 15 20 25 30 35 40 45 50 55 60


A: Albite (76-0898)
F: Potassium feldspar (76-0829)
Q: Quartz (82-0511)
K.H.L.2
(Aggregate)
Relative Intensity
°2 Theta
0 5 10 15 20 25 30 35 40 45 50 55 60


A: Albite (71-1155)
F: Potassium feldspar (76-0829)
Q: Quartz (82-0511)
D.So.L.2
(Aggregate)
Relative Intensity
°2 Theta
0 5 10 15 20 25 30 35 40 45 50 55 60


A: Albite high (83-1614)
F: Potassium feldspar (76-0829)
Q: Quartz (83-2465)
D.I.L
(Aggregate)
Relative Intensity
°2 Theta
0 5 10 15 20 25 30 35 40 45 50 55 60
Q
A,F
A
A
A
Q
A
A
Q
Q
A
Q


A: Albite (76-0898)
F: Potassium feldspar (76-0829)
Q: Quartz (79-1906)
D.I.U.2
(Aggregate)
Relative Intensity
°2 Theta
0 5 10 15 20 25 30 35 40 45 50 55 60
Q
A,F
A
A
Q
A
A
A
A
Q
Q
Q
Q
A
Q


A: Albite (71-1155)
F: Potassium feldspar (76-829)
Q: Quartz (82-0511)
D.H.L.2
(Aggregate)
Relative Intensity
°2 Theta
0 5 10 15 20 25 30 35 40 45 50 55 60
A,F
Q
A
Q
A
A
A
A
A Q
Q
Q
Q
Q

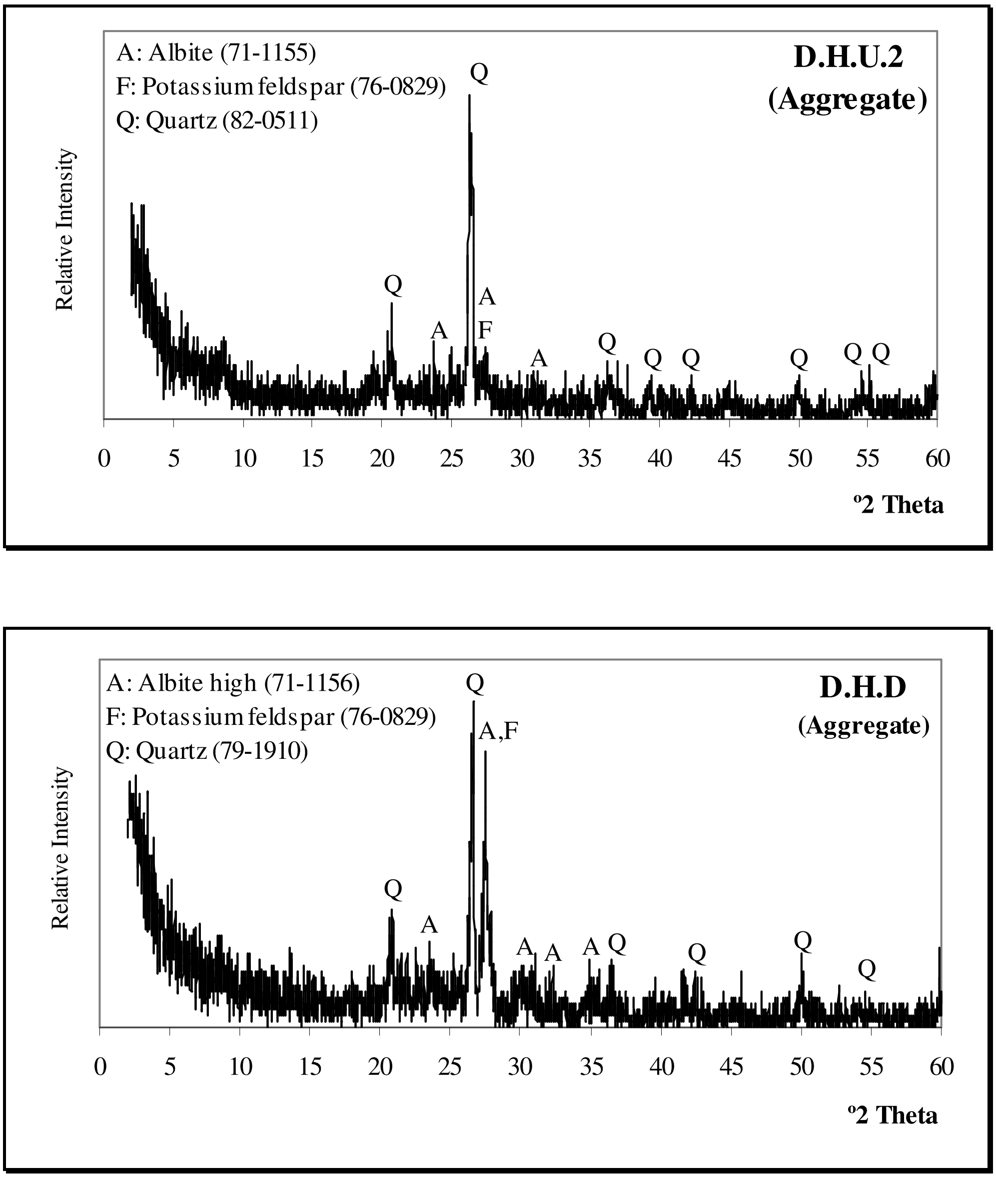
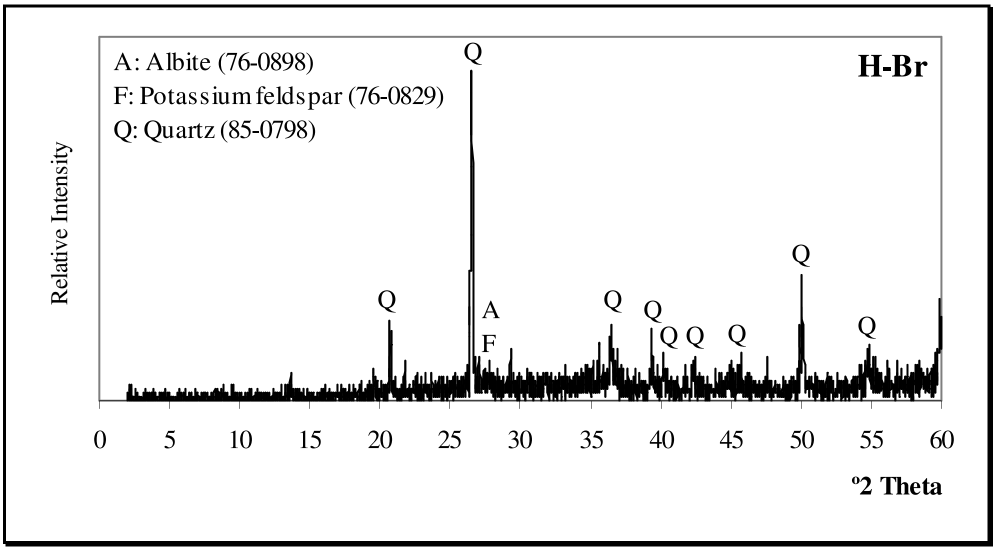
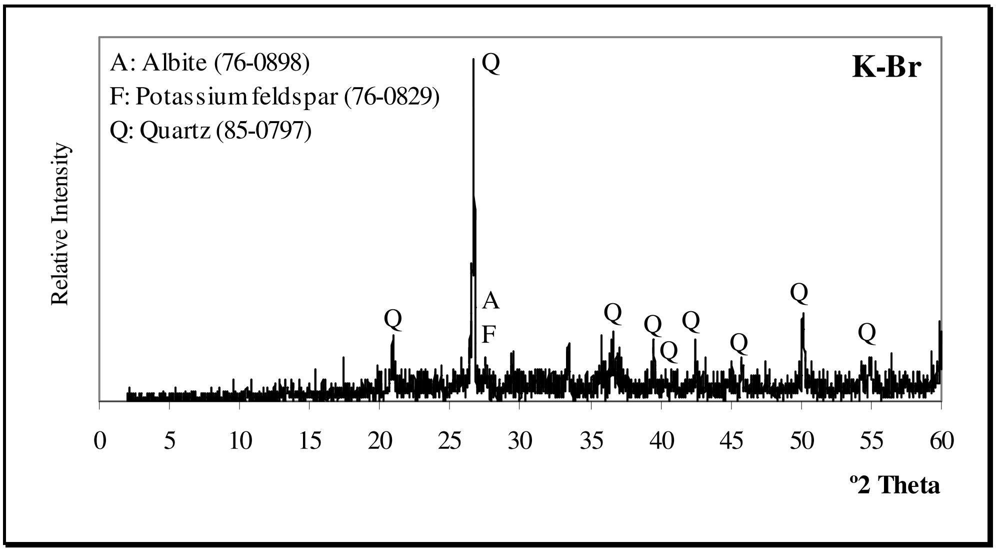


Figure 4.18. XRD patterns of some crushed brick aggregate samples





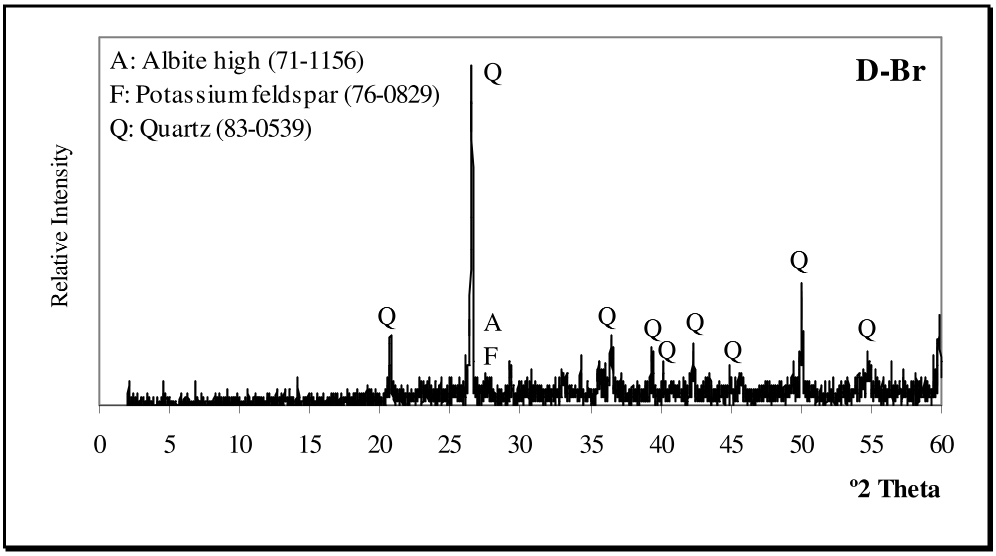


Figure 4.19. XRD patterns of building brick samples

4.5. Microstructural Properties of Horasan Plasters, Lime Plasters and Crushed Brick Aggregates

Basic microstructural properties of horasan plasters, lime plasters and crushed brick aggregates were determined by stereo microscope and SEM-EDS.

4.5.1. Microstructural Properties of Horasan Plasters

Lower level plastering of the spaces of the baths were done by one, two or three rough horasan plaster layers with a finishing layer (Figure 4.20). However, single or two layers of horasan plasters with a fine lime plaster layer were applied on upper parts (Figure 4.21). The use of multi layered plaster application could be done to protect the structure from water entry.

Boundary lines between each of horasan plaster layers were observed in the cross section of the plaster layers (Figure 4.20, 4.21). This might show that the second layers of horasan plasters had been applied after the first layers got dried. Otherwise, such a boundary line would not be observed clearly. Also, a clear line between horasan plaster layers and lime plaster was observed too (Figure 4.21, 4.22).

Horasan plasters had a stiff and homogeneous appearance. They generally had a pinkish color due to color of crushed bricks used as aggregates. This observation revealed that crushed brick aggregates and lime binder matrix had been mixed so well. However, there was a lack of information about how such a good mixing had been achieved in the Ottoman period.

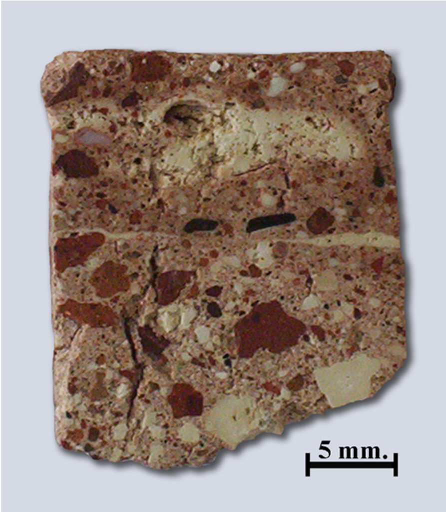


Figure 4.20. A two layered horasan plaster sample taken from lower level (D.So.U.L.1-D.So.U.L.2)

Figure 4.21. Two layers of horasan plaster with single layer of lime plaster taken from upper level (D.I.U.1-D.I.U.2-D.I.U.L)

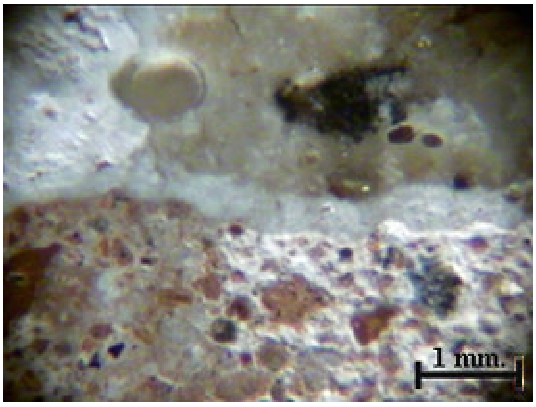
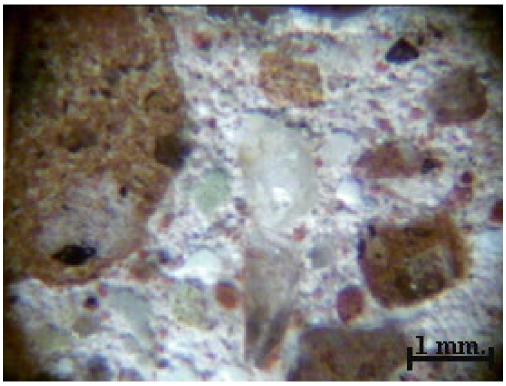


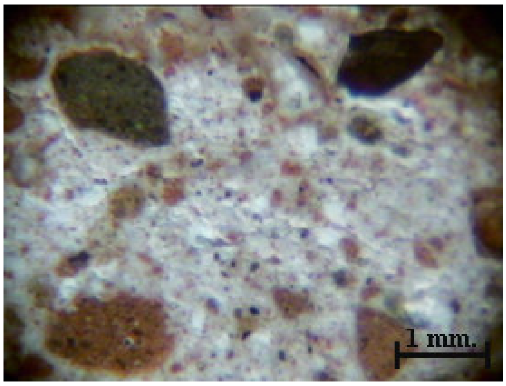
Figure 4.22. Stereo microscope image showing a horasan plaster layer with a lime plaster layer (D.H.U.2-D.H.U.L)

Strong adhesion was indicated between crushed brick aggregates and lime matrix in SEM analysis (Figure 4.23, 4.24, 4.27). In the elemental mapping images, any cracks or pores were not observed at the crushed brick-lime matrix interface (Figure 4.25, 4.26).

The width of the brick-lime interfaces found by AFM was in the range of 2-10 micrometer (10^{-3} mm.) (Figure 4.28). They were free from disconnection and very thin irregular boundaries rich in calcium (Ca), silica (Si), and alumina (Al) elements. From the brick aggregates towards the lime matrix, Ca content increased while Si and Al content decreased. In the lime matrix, Ca reached its highest content. Hydraulic compounds, such as calcium silicate hydrates and calcium alumina hydrates at the interface were most probably due to the pozzolanic reactions between lime and brick aggregates (Figure 4.29-4.31). These hydraulic compounds provide higher strength and durability to horasan mortars and plasters than those of non-hydraulic mortars and plasters (Lea 1940, Akman 1986, Tunçoku 2001).

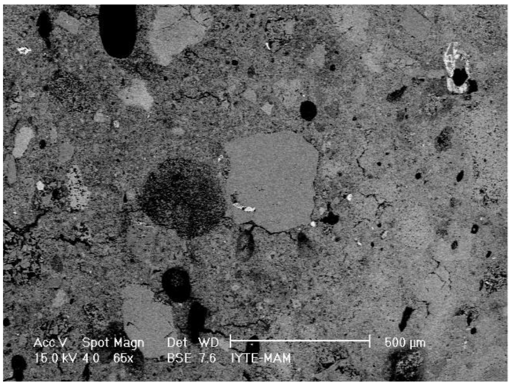


H.H.L

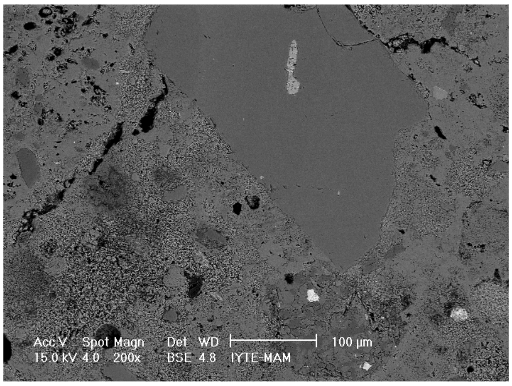


K.S.L.2

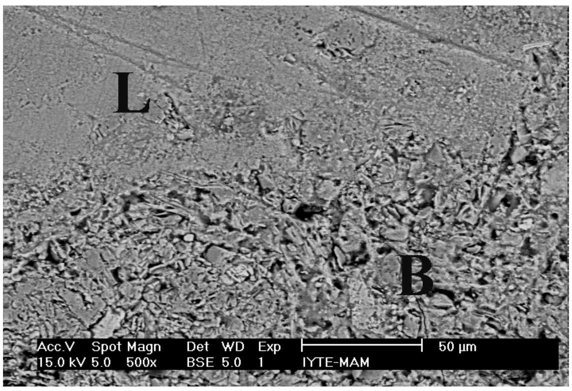
Figure 4.23. Stereo microscope images of horasan plaster samples showing good adhesion of crushed brick aggregates with lime binder



K.H.L.2 - 65x



D.H.U.2 - 200x



K.S.L.1- 500x

Figure 4.24. BSE (Backscattered electron) images showing good adhesion of crushed brick aggregate (B) with lime binder (L)

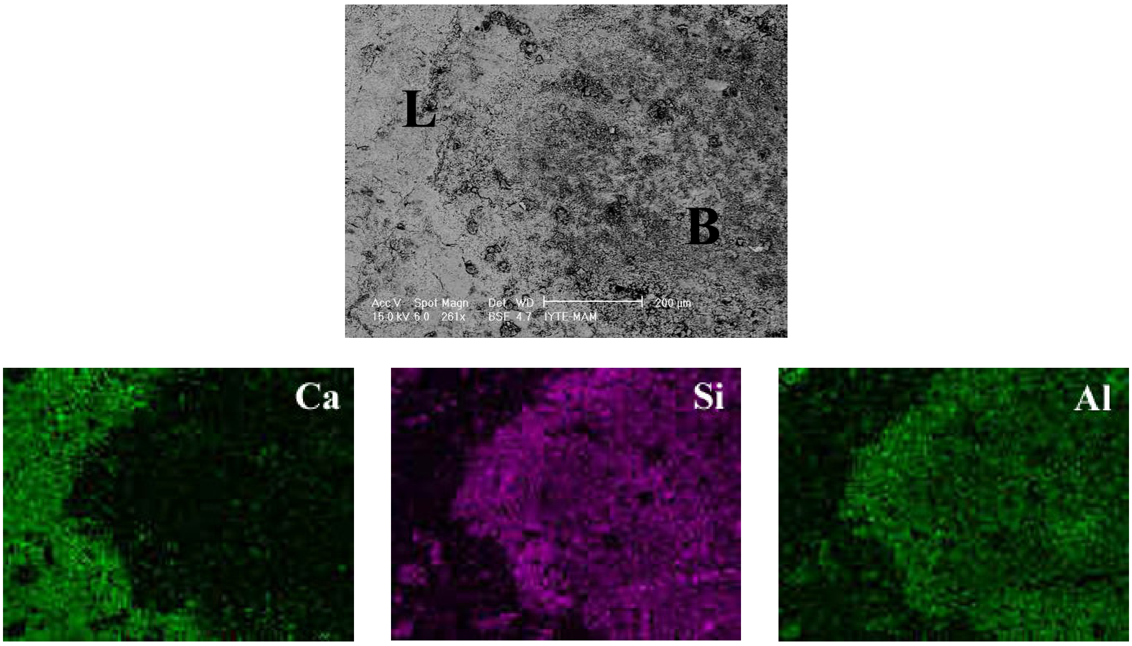


Figure 4.25. BSE and elemental mapping images of a brick aggregate (B) in lime matrix (L) (H.I.D.2)

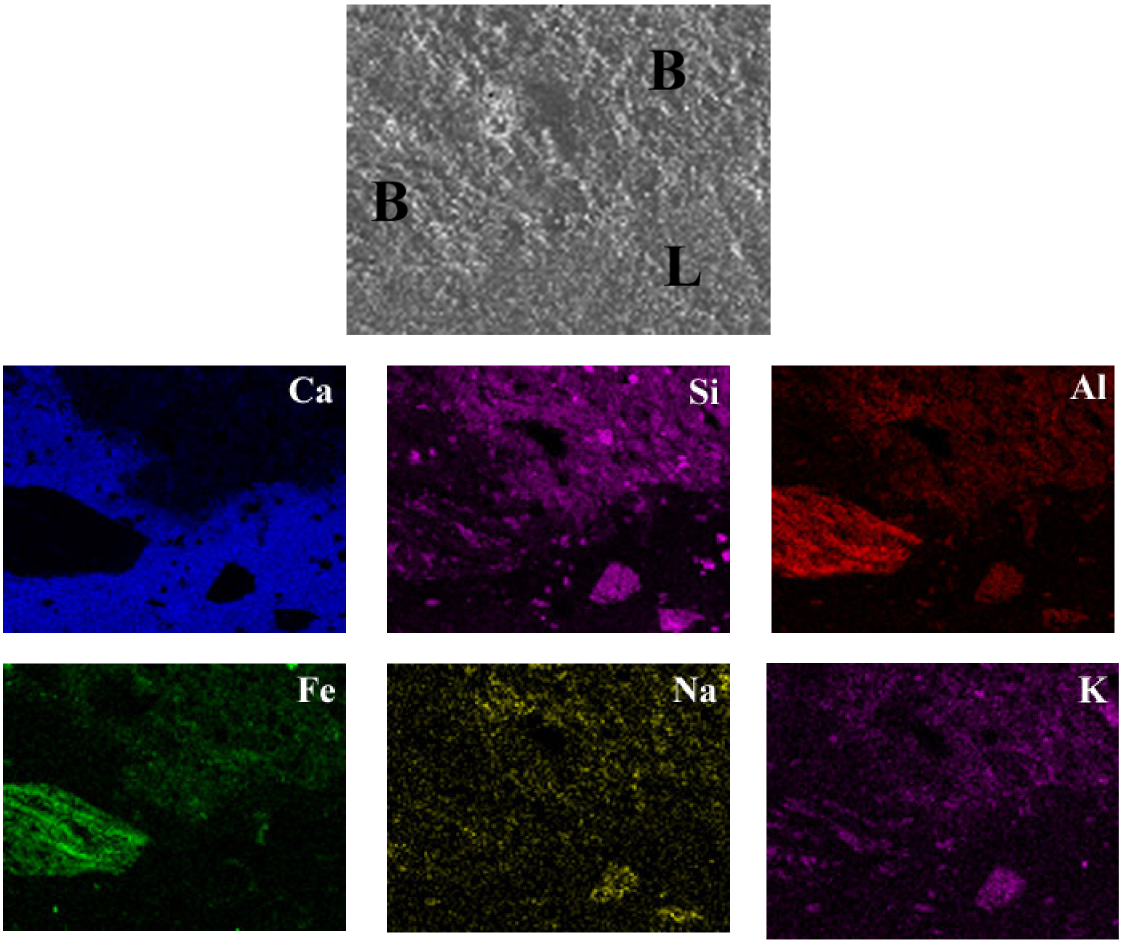
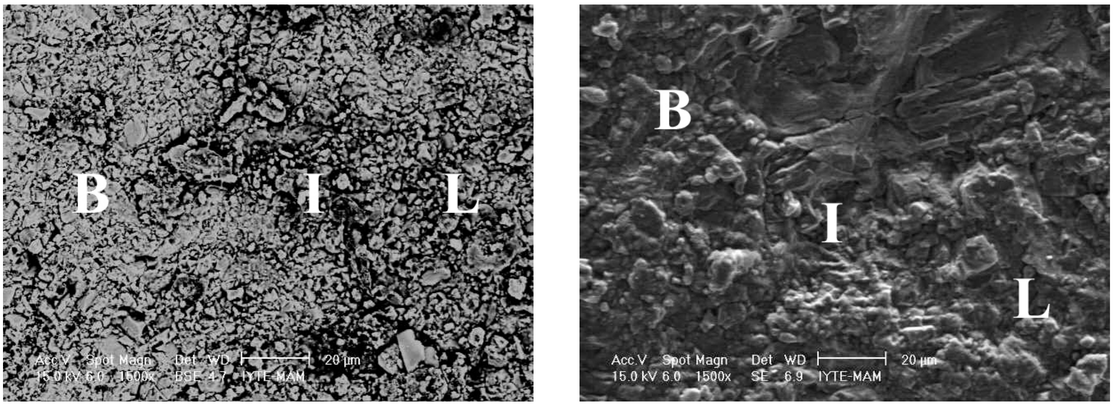
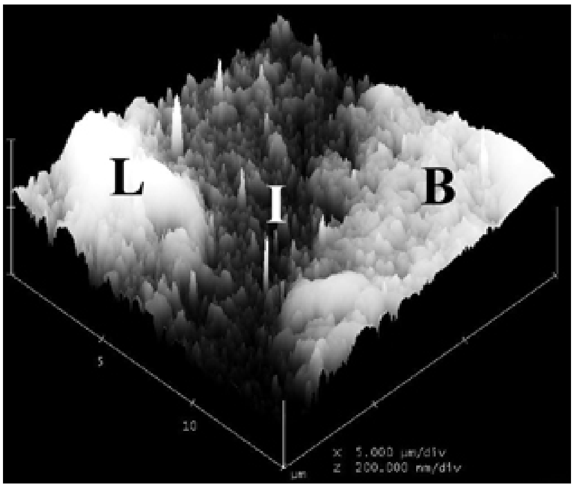


Figure 4.26. BSE and elemental mapping images of a brick aggregate (B) in lime matrix (L) (K.S.L.1)

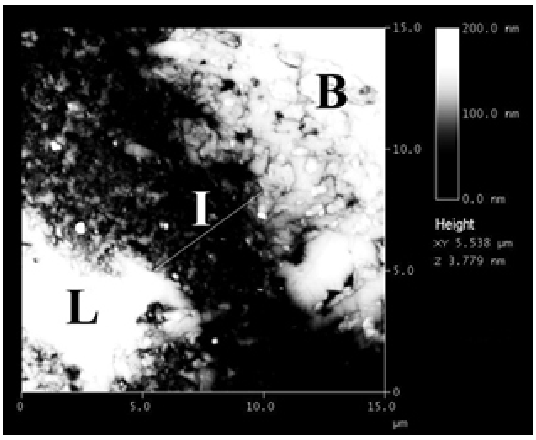


BSE - 1500x **SE – 1500x**

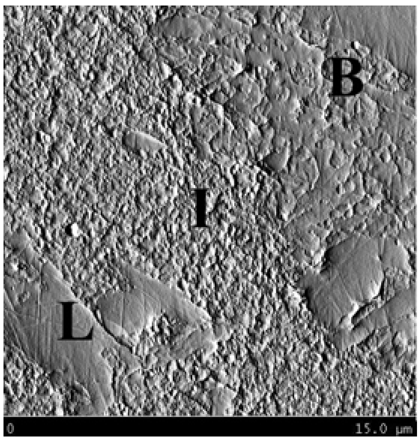
Figure 4.27. BSE (Backscattered electron) and SE (Secondary electron) images of crushed brick aggregate (B), lime matrix (L) and interface (I) showing good adhesion between them (H.I.D.2)



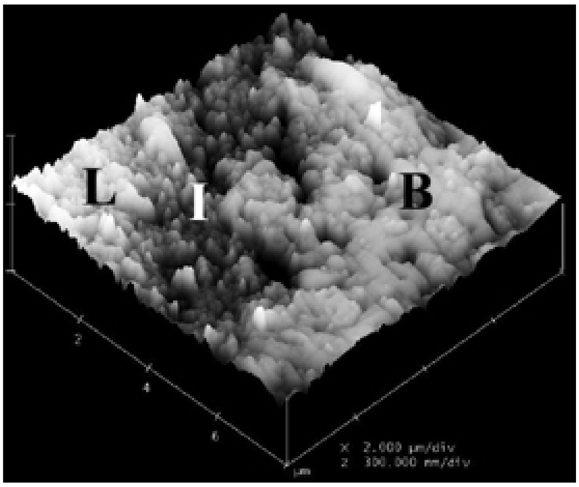
I-A



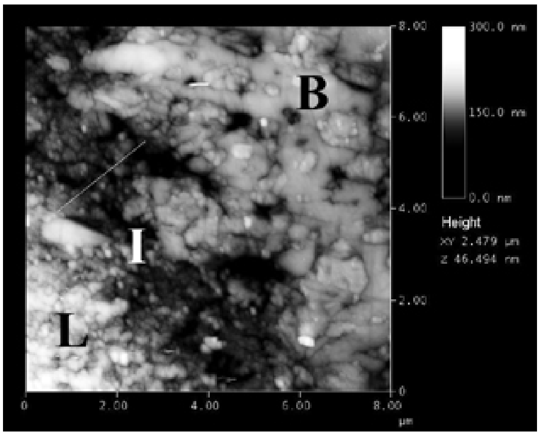
I-B



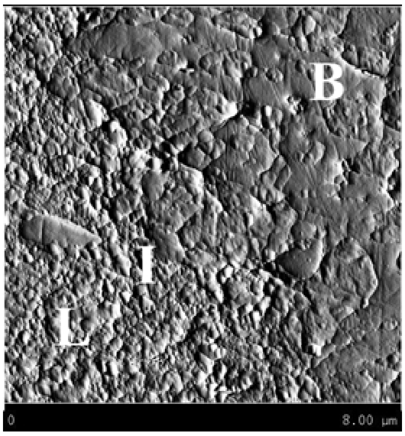
I-C



II-A

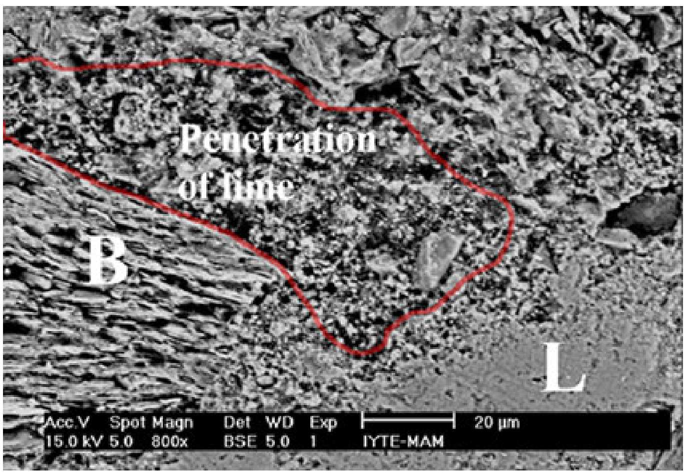


II-B



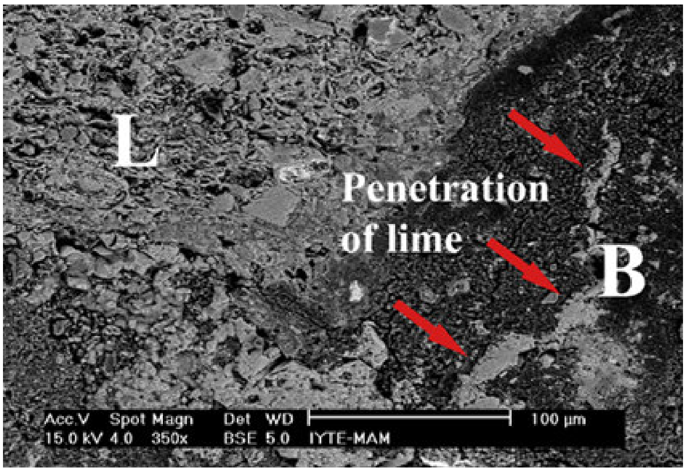
II-C

Figure 4.28. AFM images showing topography of the interface (I) between the lime binder matrix (L) and the crushed brick aggregate (B) (I-A, II-A), and the thin brick-lime interface (~2.5 micrometers) (I-B, I-C, II-B, II-C) (K.H.L.2)



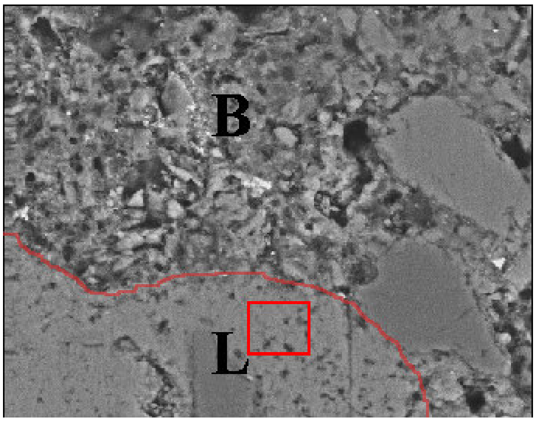
800x

Figure 4.29. BSE image showing penetration of lime (L) to the brick aggregate (B) (K.S.L.1)

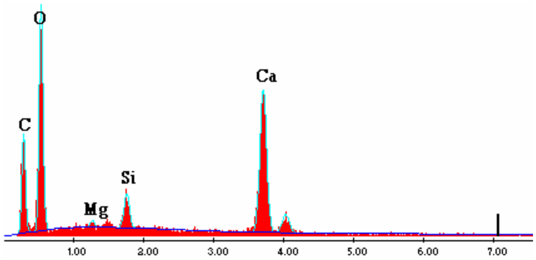


350x

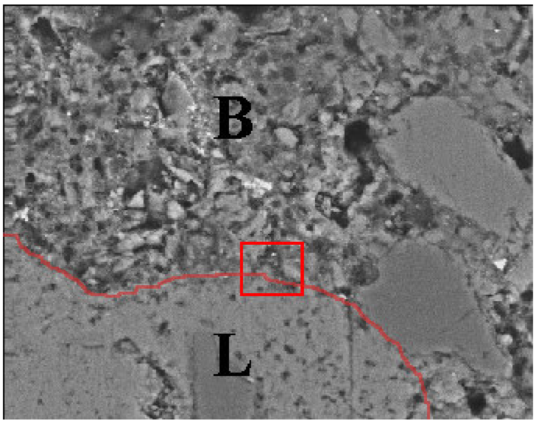
Figure 4.30. BSE image showing penetration of lime (L) to the brick aggregate (B) (H.H.U)



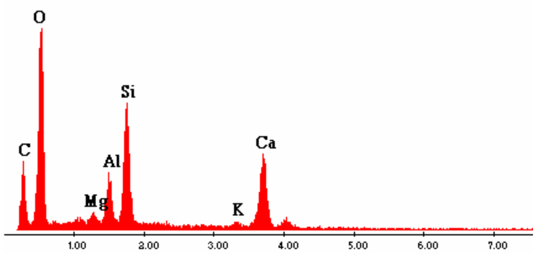
(I-A)



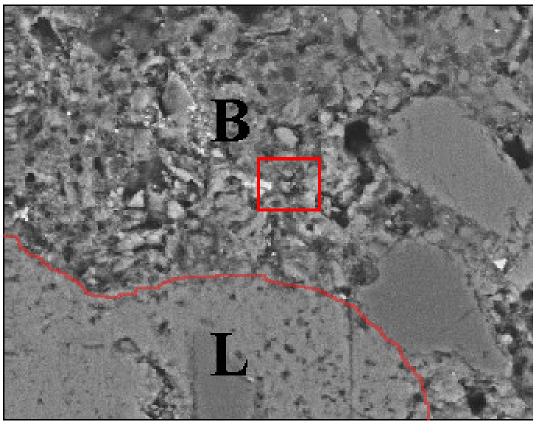
(I-B)

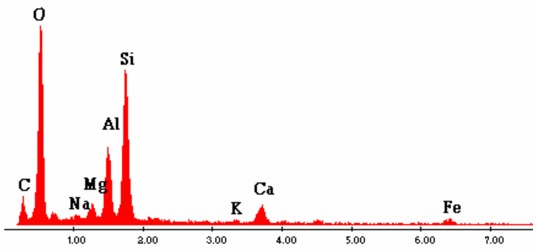


(II-A)



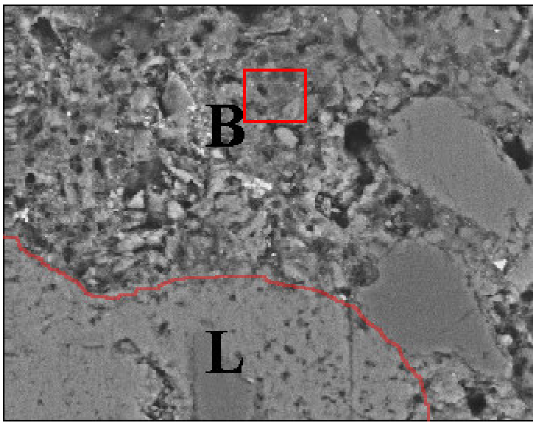
(II-B)

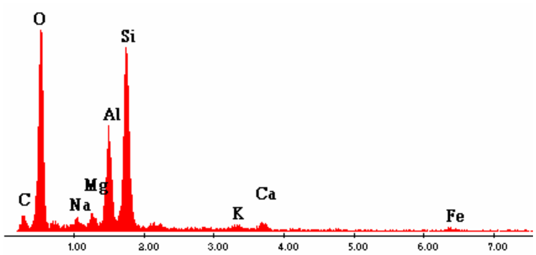




(III-B)

(III-A)





(IV-B)

(IV-A)

Figure 4.31. BSE images (I-A, II-A, III-A, IV-A) showing crushed brick aggregate and lime matrix and EDS spectrums (I-B, II-B, III-B, IV-B) showing decrease of calcium content from lime matrix to crushed brick aggregate (D.H.U.2)

4.5.1.1. Porosity Values of Finishing Layers Determined by SEM

Porosity values of horasan and lime plasters and building bricks had been determined by using RILEM standard test methods (RILEM 1980). However, it was not possible to determine the porosity values of the finishing layers with RILEM method since they were so thin to use this standard. Hence, porosity values of finishing layers were determined by using SEM.

It was determined that finishing layers had about 6 % pore area while horasan plaster taken below the surface had 15 % (Figure 4.32, 4.33). These values show that finishing layers were less porous which provided a water-proof surface that prevented liquid water entry into the bath structure.

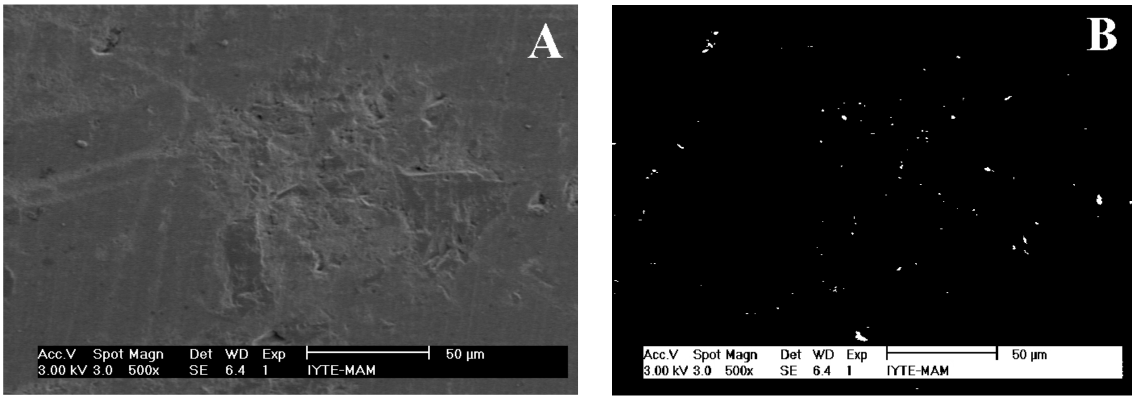


Figure 4.32. SE images of finishing layer sample taken from the surface of horasan plaster, showing the general texture (A) and the pore areas (B) which are white in the image (K.S.L.1)

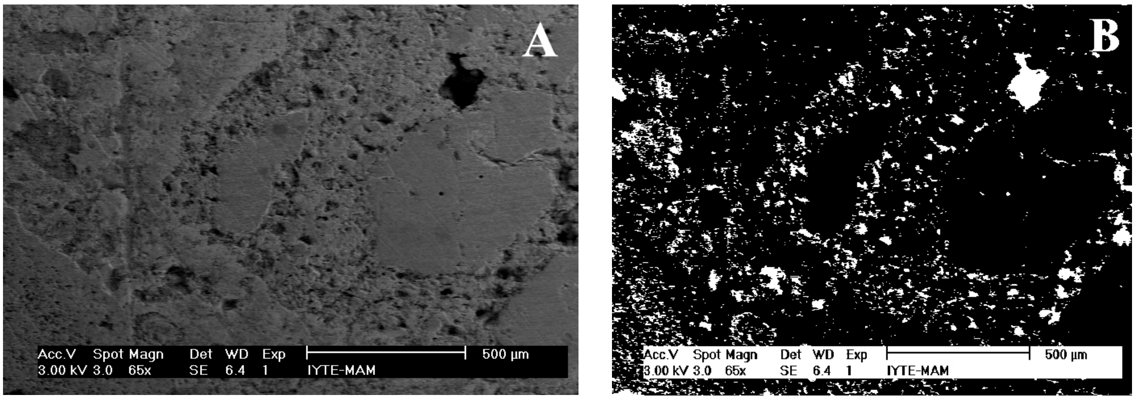
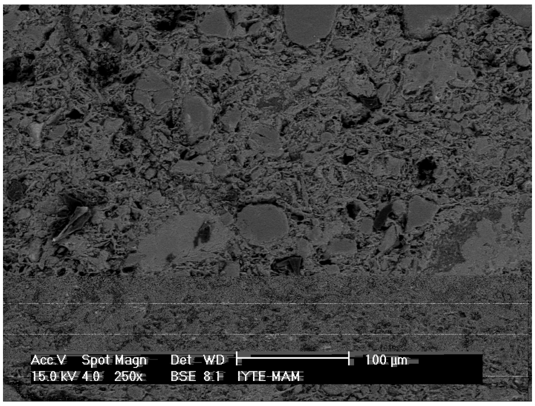


Figure 4.33. SE images of horasan plaster sample taken below the surface, showing the general texture (A) and the pore areas (B) which are white in the image (K.S.L.1)

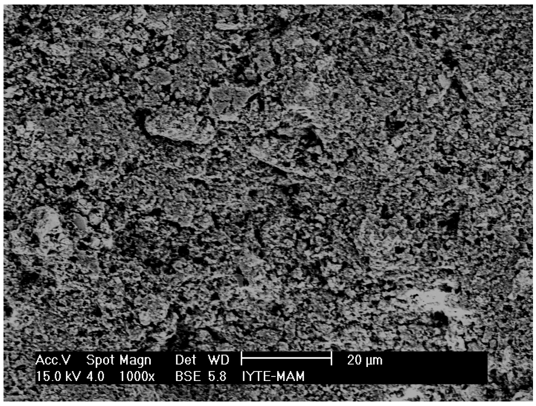
4.5.1.2. Microstructural Characteristics of Crushed Brick Aggregates

Pore area percents of crushed brick aggregate and lime binder were also found by SEM. The porosity values of brick aggregates and lime binder were found about 18 % and 34 % (Figure 4.34, 4.35).



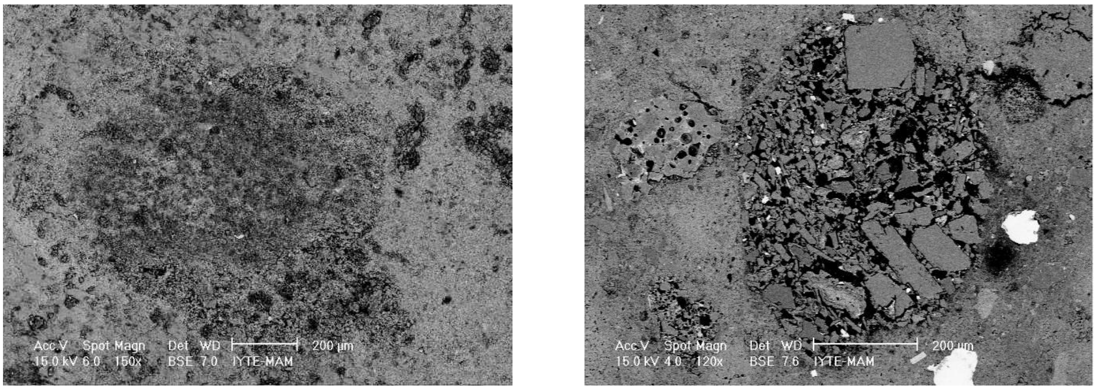
Pore area percent – 18 %

Figure 4.34. BSE image (250x) of brick aggregate (H.H.U)



Pore area percent – 34 %

Figure 4.35. BSE image (10000x) of lime matrix (H.H.U)

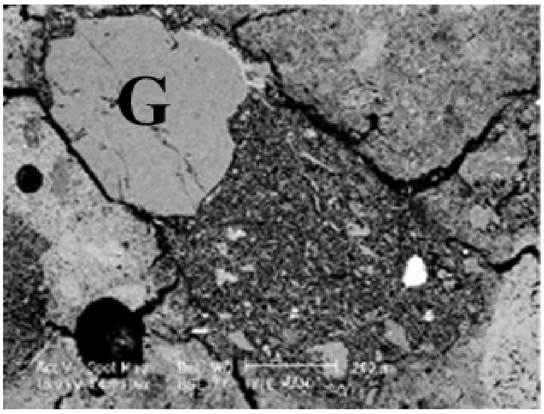


150x **120x**

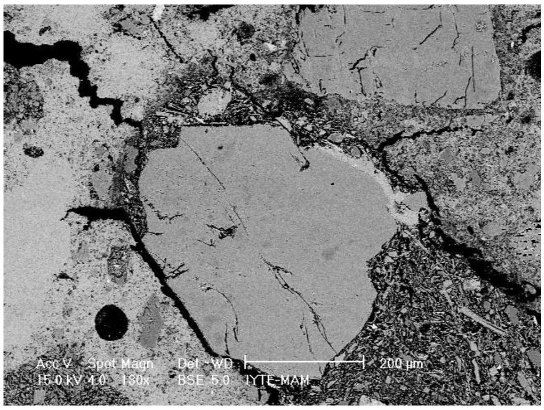
Figure 4.36. BSE images of porous crushed brick used as aggregate within the matrix in horasan plaster (H.I.D.2)

Some of the brick aggregates contained grog particles which can be defined as granular materials made from crushed brick, rock or other pre-fired ceramic products (Figure 4.37). Grog particles are generally added to the mixture of raw materials of bricks to reduce drying and firing shrinkage of brick and to increase stability during firing process. EDS analyses revealed that grog particles were composed of mostly silicon, aluminum, calcium and sodium (Figure 4.37).

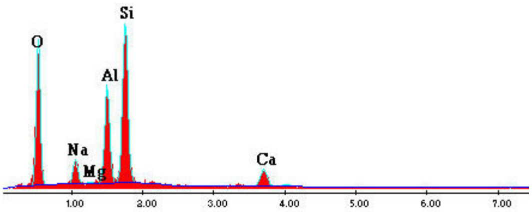
Crushed brick aggregates contained mainly feldspar (Figure 4.38), quartz (Figure 4.39) and amorphous substances (Figure 4.40). Amorphous substances which were consisted of mainly silicon and aluminum could show the presence of metakaolin derived from the use kaolinite in the raw materials of brick aggregates (Figure 4.40). Small quantity of iron oxide particles were also been observed in their composition (Figure 4.41).



BSE-100x



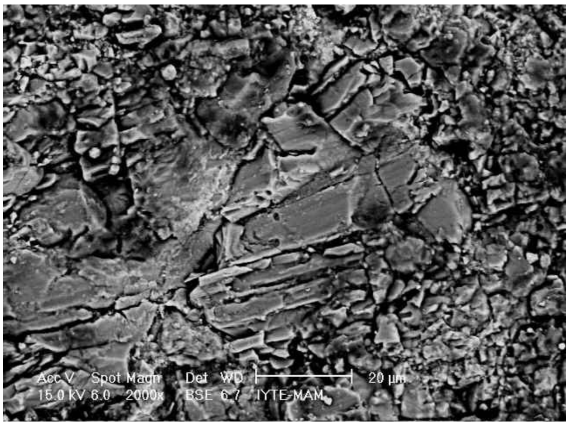
BSE-130x



EDS spectrum

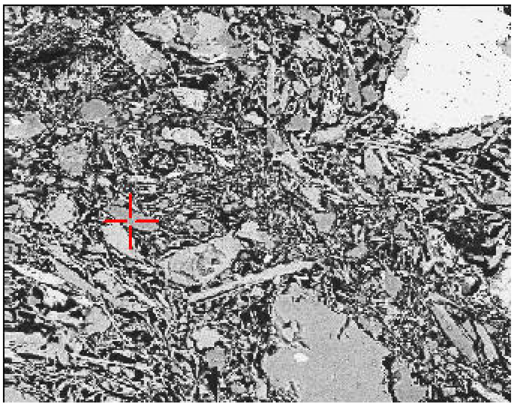
Element	Wt. %
O	43.5
Na	5.4
Mg	0.5
Al	15.5
Si	28.9
Ca	6.3
Total	**100.0**

Figure 4.37. BSE images, EDS spectrum and elemental composition of grog particle (G) in brick aggregate (K.H.L.2)

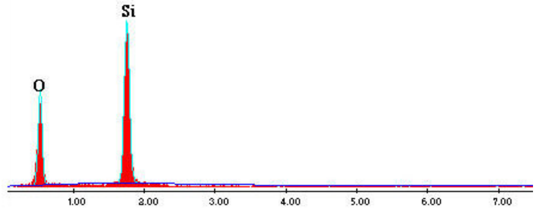


2000x

Figure 4.38. BSE image of feldspar crystals in brick aggregate (H.I.D.2)



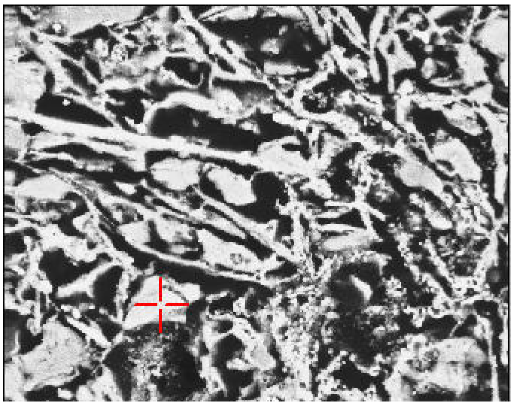
(A)



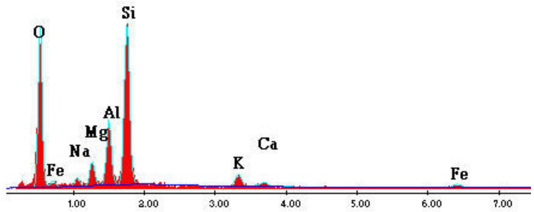
(B)

(C)	Element	Wt. %
	O	49.8
	Si	50.2
	Total	**100.0**

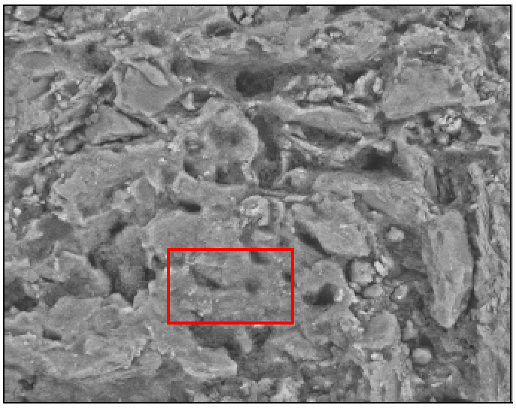
Figure 4.39. BSE image (A) of crushed brick aggregate, EDS spectrum (B) and elemental composition (C) of quartz particles in crushed brick aggregate (K.H.L.2)



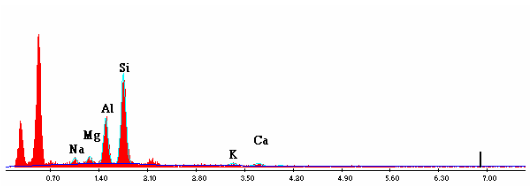
K.H.L.2 - BSE



K.H.L.2 – EDS spectrum



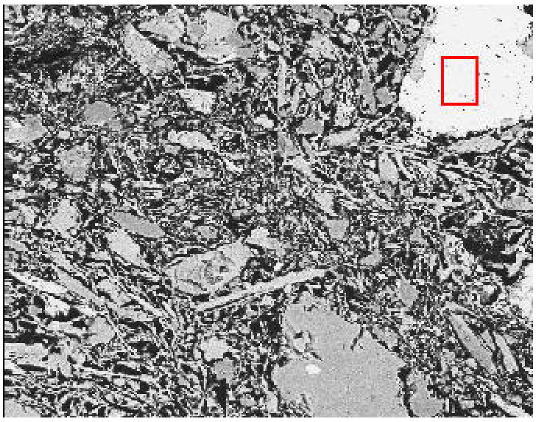
H.H.U - BSE



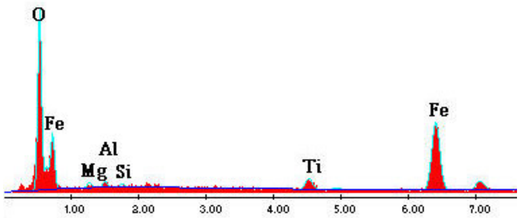
H.H.U – EDS spectrum

Element	Wt. %
Na	3.0
Mg	3.7
Al	23.0
Si	62.9
K	3.3
Ca	4.1
Total	**100.0**

Figure 4.40. BSE images, EDS spectrums and elemental composition of amorphous substances composed of mainly silicon and aluminum which can show the presence of metakaolin in crushed brick aggregate



(A)



(B)

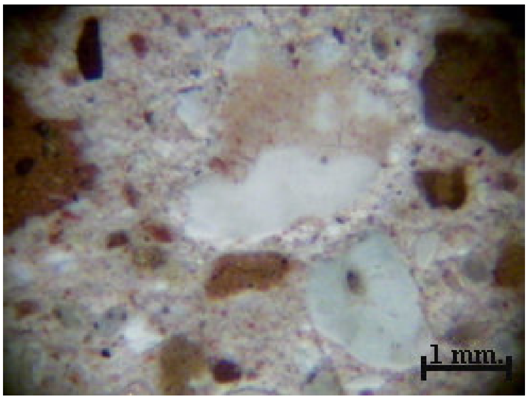
(C)

Element	Wt. %
O	28.7
Mg	1.1
Al	1.1
Si	0.5
Ti	4.2
Fe	64.5
Total	**100.0**

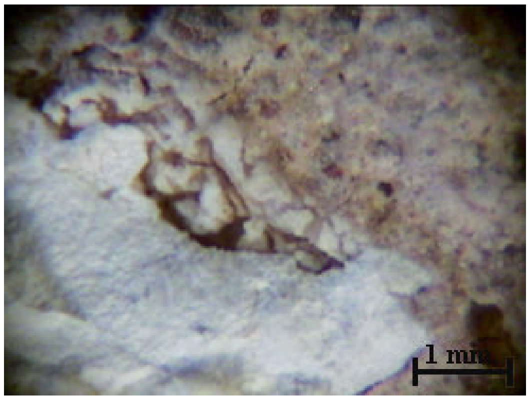
Figure 4.41. BSE image (A) of brick aggregate, EDS spectrum (B) and elemental composition (C) of iron oxide particles in crushed brick aggregate (K.H.L.2)

4.5.1.3. Properties of Lime Binder Used in the Preparation of Horasan Plasters

Small, white, round and soft pieces called “white lumps” were observed in all plaster samples (Figure 4.42). They represent the binding material used in the mortars and plasters (Baronia et. al. 1997b, Biscontin et. al. 2002) Mineralogical compositions of the white lumps were determined by XRD analyses. Strong calcite peaks were observed in their XRD patterns (Figure 4.43). SEM-EDS analyses indicated that the white lumps horasan plasters were composed of calcite crystals containing high amounts of calcium oxide over 90 % (Figure 4.43-4.45). These analysis results revealed that pure lime was used in the preparation of the plasters.

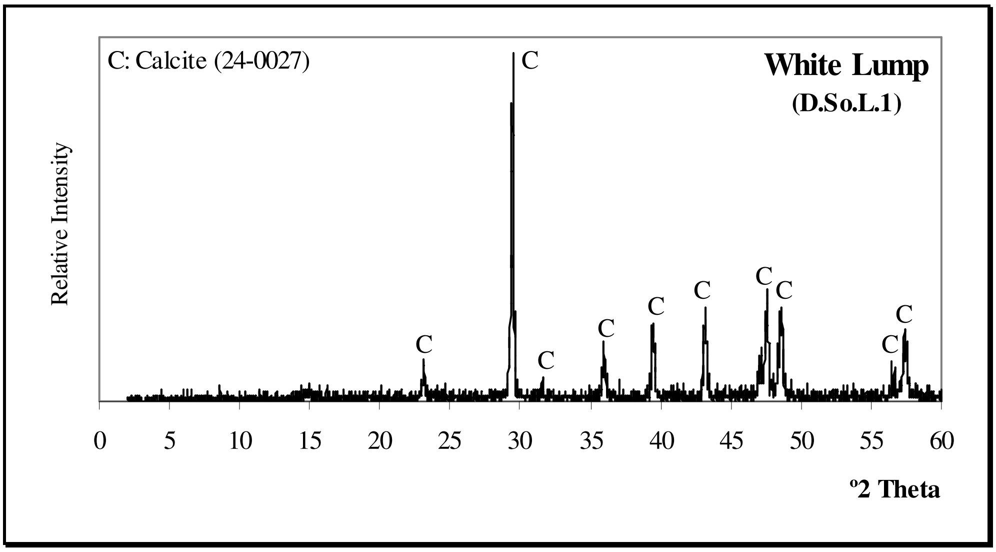


H.H.L



D.So.L.1

Figure 4.42. Stereo microscope images of white lumps in horasan plasters

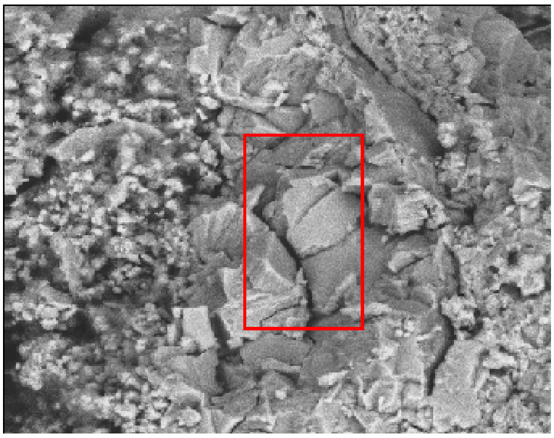


XRD pattern

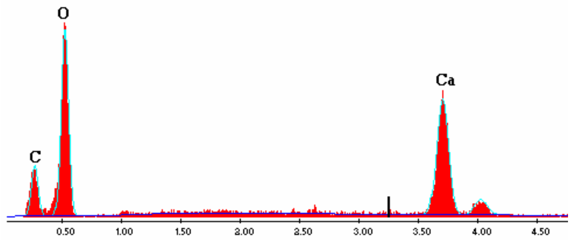
Oxide	**%**
CaO	93.68
SiO_2	3.96
Al_2O_3	2.35
Total	**100.00**

Elemental composition (%)

Figure 4.43. XRD pattern and elemental composition of a white lump sample



(A)

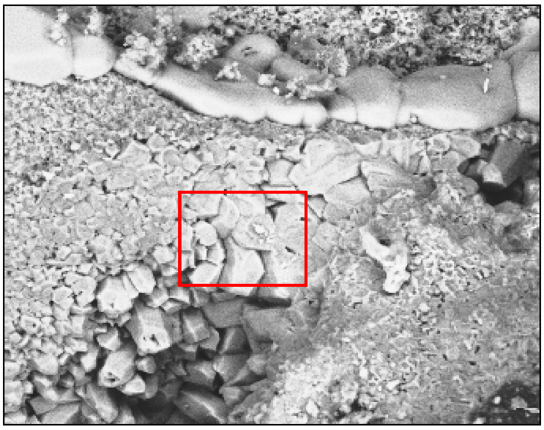


(B)

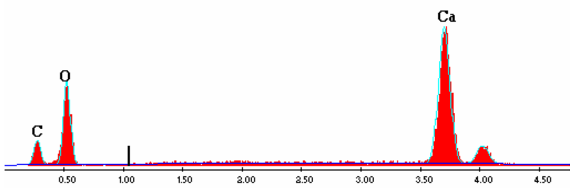
(C)

Element	Wt. %
C	10.3
O	44.6
Ca	45.1
Total	**100.0**

Figure 4.44. BSE image (A), EDS spectrum (B) and elemental composition (C) of white lump in horasan plaster matrix (K.S.L.1)



(A)



(B)

(C)

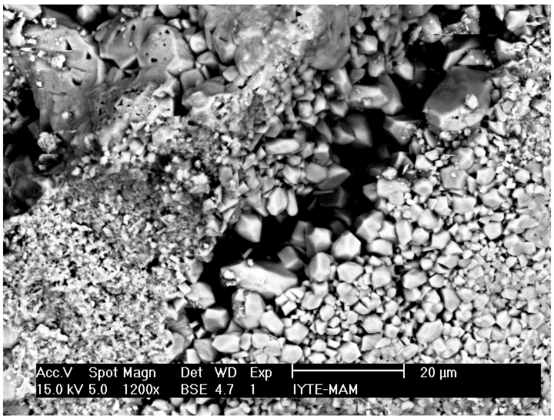
Element	Wt. %
C	8.3
O	49.5
Ca	42.2
Total	**100.0**

Figure 4.45. BSE (Backscattered electron) image (A) and EDS spectrum of white lump in horasan plaster (K.S.L.1)

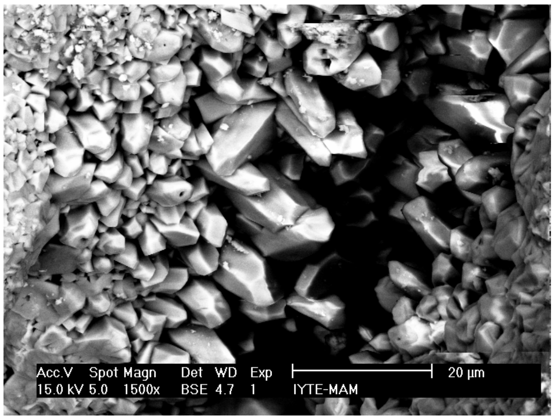
4.5.1.4. Calcite Deposition in the Pores of Horasan Plasters and Crushed Brick Aggregates

Calcite crystals were observed in the pores of horasan plasters (Figure 4.46) and crushed brick aggregates (Figure 4.47-4.48). These crystals were thought to be precipitated by the dissolution of carbonated lime in the humid atmosphere of the bath.

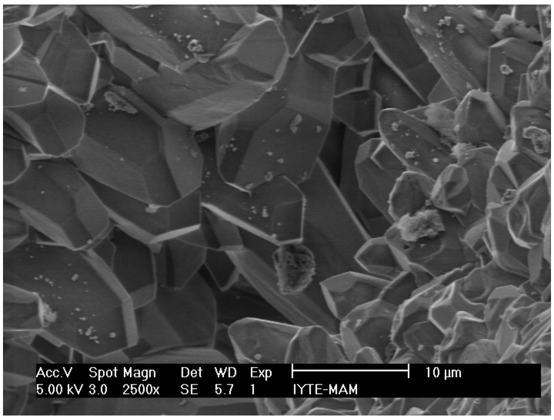
It may be suggested that porous brick aggregates were ideal materials for the durability of plasters because they might prevent deterioration caused by the dissolution and precipitation of carbonated lime (Böke et. al. 2004).



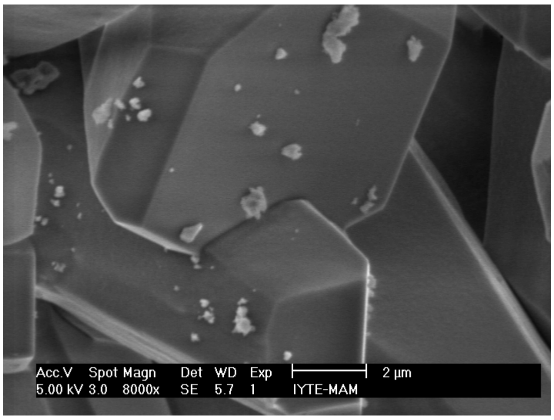
BSE-1200x



BSE-1500x

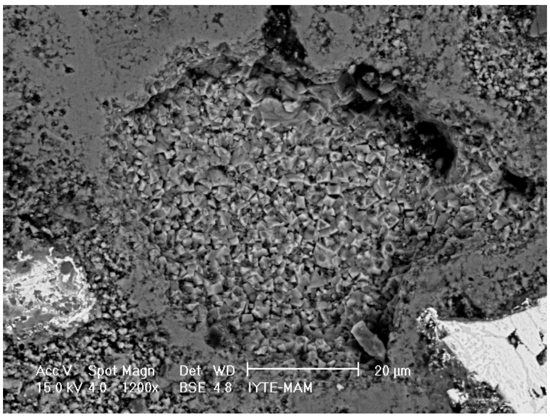


SE-2500x

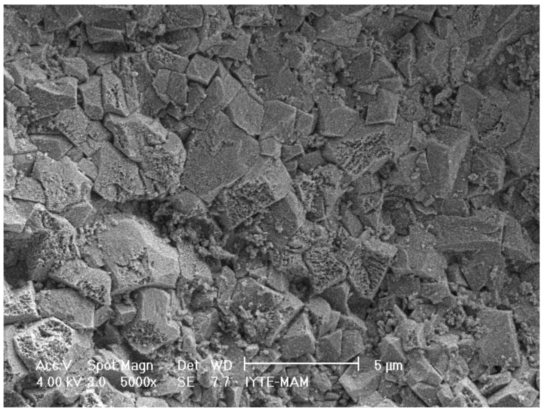


SE-8000x

Figure 4.46. BSE and SE images of calcite crystals precipitated in pores of horasan plaster matrix (K.S.L.1)

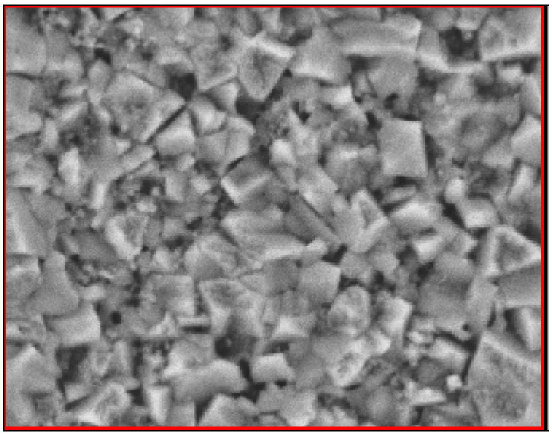


1200x

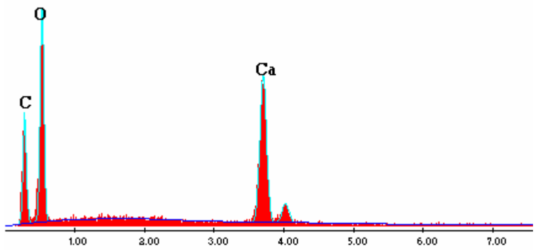


5000x

Figure 4.47. BSE images of calcite crystals precipitated in pores of a crushed brick aggregate (D.H.U.2)



(A)

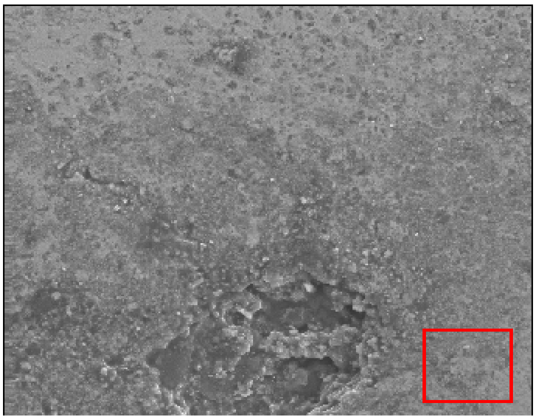


(B)

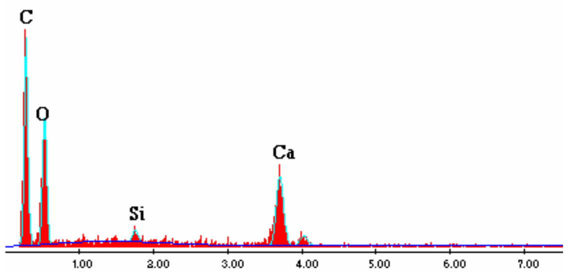
Figure 4.48. BSE image (A) and EDS spectrum of calcite crystals precipitated in pores of a crushed brick aggregate (D.H.U.2)

4.5.2. Microstructural Properties of Lime Plasters Used on Upper Level Horasan Plasters

Mineralogical compositions of the lime plasters were determined by XRD analyses. Strong calcite and weak quartz peaks were observed in their XRD patterns (Figure 4.17). EDS analyses indicated that the plasters were composed of mostly calcium oxide (Figure 4.49).



(A)



(B)

Figure 4.49. BSE image (A) and EDS spectrum of lime plaster layer which was composed of mostly $CaCO_3$ (D.H.U.L)

Lime plasters were lost of their strength, hardness and hydro-thermal stability by the dissolution and precipitation of carbonated lime in humid and hot atmosphere of the baths (Figure 4.50, 4.51). Due to the subsequent dissolution and precipitation reaction, several deposited calcite layers were observed (Figure 4.52, 4.53). Layers were very porous and easily crumble.

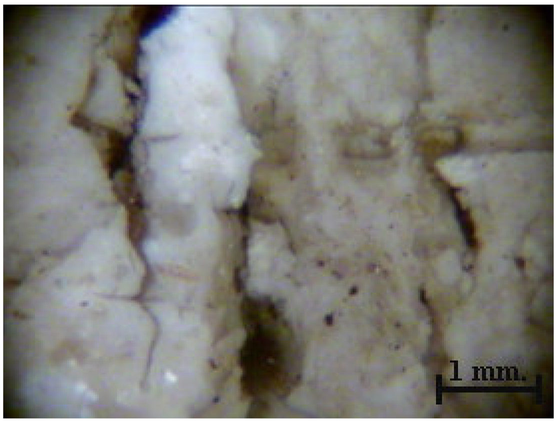


Figure 4.50. Stereo microscope image of cracks observed in lime plaster layer (K.H.U.L)

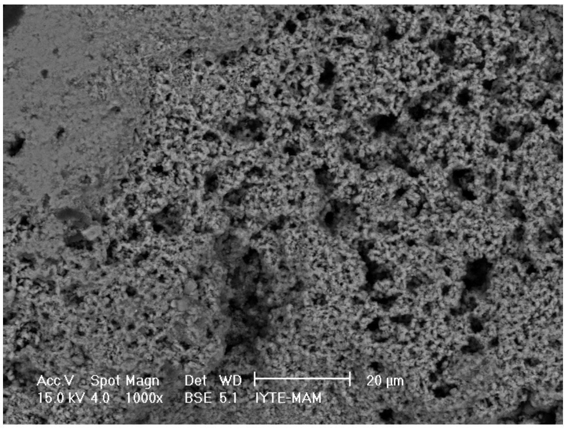
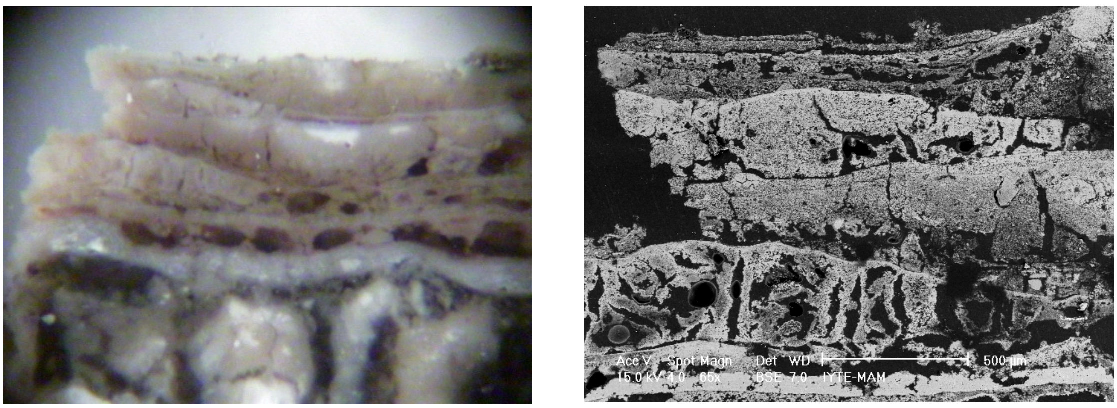
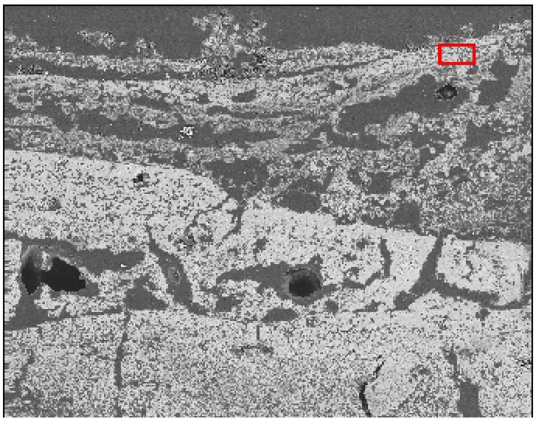


Figure 4.51. BSE image (1000x) of much porous lime plaster formed by the dissolution of $CaCO_3$ (D.H.U.L)

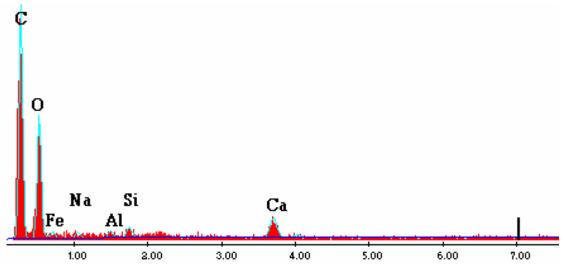


(A) **(B)**

Figure 4.52. Stereo microscope (A) and BSE (65X) (B) images of deposited calcite layers due to dissolution and precipitation of lime (H.H.U)



(A)



(B)

Figure 4.53. BSE image (A) and EDS spectrum (B) of deposited calcite layers (H.H.U)

4.6. Chemical Compositions of Horasan Plasters, Lime Plasters and Crushed Brick Aggregates Determined by SEM-EDS Analyses

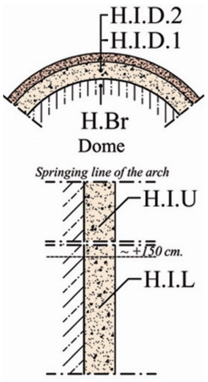
The elemental composition analyses revealed that horasan plasters were consisted of high amounts CaO, SiO_2, Al_2O_3 and low amounts of Fe_2O_3, MgO, Na_2O (Table 4.1, 4.2, 4.3). Calcium oxide was derived from carbonated lime, and SiO_2 and Al_2O_3 were derived from brick powders.

The elemental composition analyses of crushed brick aggregates and building bricks indicated that all the bricks were mainly consisted of high amounts of SiO_2, Al_2O_3 and low amounts of Fe_2O_3, MgO, Na_2O, K_2O, CaO (Table 4.1, 4.2, 4.3). However, the amounts of Fe_2O_3 in building bricks were found to be higher than that of all crushed bricks. Similar results have also been found in studies carried out the brick aggregates used in some historic Ottoman bath plasters and domes in Bursa and Edirne (Böke et. al. 2004).

Results of the elemental composition analyses of lime plasters showed that lime plasters were mainly composed of high amounts of CaO (Table 4.1, 4.2 and 4.3). This showed the use of high amounts of pure lime in the preparation of lime plasters.

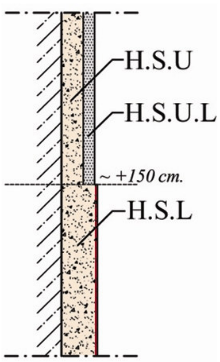
Table 4.1. Elemental compositions (%) of some horasan plaster, brick aggregates, lime plaster and building brick samples of Hersekzade Bath

Samples collected from the ılıklık space



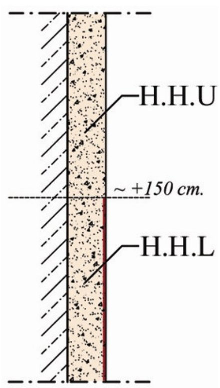
Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
H.I.D.2	51.2 ± 0.7	2.0 ± 0.0	27.2 ± 1.1	10.3 ± 0.2	4.7 ± 0.6	1.9 ± 0.2	2.1 ± 0.2	0.7 ± 0.4
H.I.D.2 (agg.)	1.4 ± 0.4	1.3 ± 0.3	78.2 ± 0.6	10.1 ± 0.3	4.5 ± 0.3	2.0 ± 0.4	2.5 ± 0.2	–
H.I.L	39.6 ± 1.4	4.9 ± 0.4	28.3 ± 0.2	11.3 ± 0.2	3.0 ± 0.3	3.5 ± 0.6	1.1 ± 0.1	8.3 ± 0.6
H.I.L (agg.)	1.1 ± 0.4	–	92.6 ± 0.8	4.2 ± 0.5	–	1.2 ± 0.2	0.8 ± 0.0	–
H.Br	1.6 ± 0.4	3.0 ± 0.1	54.9 ± 0.7	24.0 ± 0.2	9.3 ± 0.6	2.0 ± 0.1	3.5 ± 0.1	1.7 ± 0.2

Samples collected from the sıcaklık space



Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
H.S.L	22.7 ± 0.6	4.7 ± 0.3	50.9 ± 1.3	13.5 ± 0.3	3.3 ± 0.4	1.9 ± 0.1	1.8 ± 0.1	1.2 ± 1.0
H.S.L (agg.)	1.1 ± 0.1	0.9 ± 0.2	81.3 ± 1.2	8.8 ± 0.3	3.4 ± 0.4	2.3 ± 0.4	2.1 ± 0.2	–
H.S.U.L	86.6 ± 0.7	1.9 ± 0.2	6.9 ± 0.3	2.1 ± 0.1	–	0.7 ± 0.2	–	1.8 ± 0.3

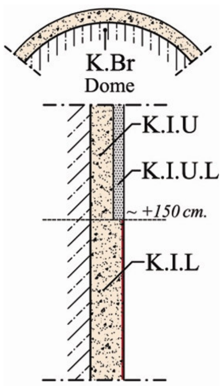
Samples collected from the halvet space



Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
H.H.L	26.4 ± 0.4	3.0 ± 0.2	43.8 ± 0.7	16.6 ± 0.4	4.1 ± 0.4	2.9 ± 0.1	1.6 ± 0.1	1.5 ± 0.3
H.H.L (agg.)	0.8 ± 0.1	0.6 ± 0.6	87.6 ± 0.8	5.8 ± 0.3	2.3 ± 0.2	1.9 ± 0.3	1.0 ± 0.1	–

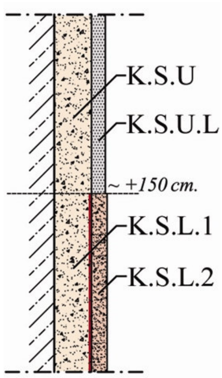
Table 4.2. Chemical compositions (%) of some horasan plaster, crushed brick aggregates of horasan plaster, lime plaster and building brick samples of Kamanlı Bath

Samples collected from the ılıklık space



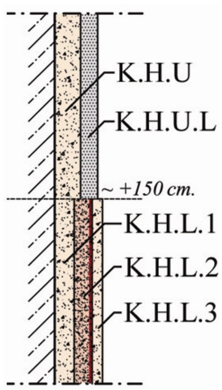
Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
K.I.L	29.4 ± 0.5	2.8 ± 0.1	43.6 ± 0.3	13.7 ± 0.3	5.0 ± 0.4	2.5 ± 0.1	2.5 ± 0.2	0.5 ± 0.1
K.I.L (agg.)	1.2 ± 0.1	1.7 ± 0.3	77.3 ± 0.6	10.0 ± 0.1	5.3 ± 0.5	2.6 ± 0.4	1.9 ± 0.1	–
K.I.U.L	87.3 ± 1.6	1.7 ± 0.4	3.3 ± 0.1	2.5 ± 0.5	–	1.5 ± 0.4	–	3.7 ± 0.6
K.Br	3.7 ± 0.3	2.6 ± 0.1	59.2 ± 0.6	20.3 ± 0.4	8.6 ± 0.5	2.0 ± 0.2	3.7 ± 0.2	–

Samples collected from the sıcaklık space



Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
K.S.L.2	31.1 ± 1.3	2.5 ± 0.3	41.5 ± 0.6	13.7 ± 0.5	5.2 ± 0.9	2.6 ± 0.4	1.7 ± 0.1	1.8 ± 0.3
K.S.L.2 (agg.)	1.5 ± 0.1	1.7 ± 0.1	83.4 ± 1.4	6.8 ± 0.4	4.1 ± 0.8	1.6 ± 0.1	1.0 ± 0.1	–
K.S.U.L	88.0 ± 1.5	4.3 ± 0.3	5.0 ± 0.6	2.7 ± 0.6	–	–	–	–

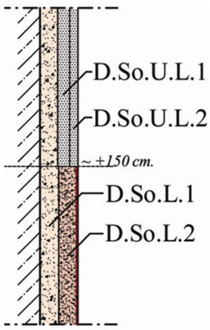
Samples collected from the halvet space



Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
K.H.L.2	55.3 ± 1.0	2.6 ± 0.2	24.9 ± 0.3	8.6 ± 0.1	3.7 ± 0.4	2.5 ± 0.1	1.9 ± 0.0	0.5 ± 0.2
K.H.L.2 (agg.)	1.7 ± 0.3	1.8 ± 0.2	68.5 ± 0.7	14.2 ± 0.1	7.2 ± 0.2	3.5 ± 0.1	3.1 ± 0.1	–
K.H.U.L	78.9 ± 1.1	3.7 ± 0.2	4.3 ± 0.2	3.4 ± 0.1	2.8 ± 1.0	2.3 ± 0.2	1.2 ± 0.2	3.5 ± 0.4

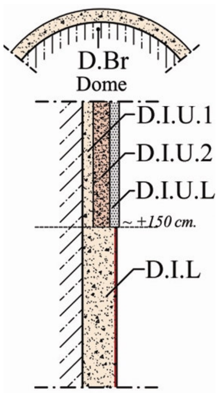
Table 4.3. Chemical compositions (%) of some horasan plaster, crushed brick aggregates of horasan plaster, lime plaster and building brick samples of Düzce Bath

Samples collected from the soyunmalık space



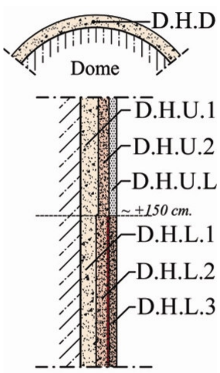
Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
D.So.U.L.1	91.3 ±1.0	1.7 ± 0.2	3.2 ± 0.2	2.0 ± 0.6	–	1.7 ± 0.3	–	–

Samples collected from the ılıklık space



Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
D.I.L	38.7 ± 1.1	2.9 ± 0.1	38.2 ± 1.2	11.8 ± 0.2	4.0 ± 0.1	2.1 ± 0.2	2.3 ± 0.3	–
D.I.L. (agg.)	1.6 ± 0.0	1.5 ± 0.2	80.9 ± 0.4	7.9 ± 0.3	4.7 ± 0.5	1.9 ± 0.2	1.6 ± 0.2	–
D.I.U.2	43.6 ± 0.3	1.9 ± 0.3	36.1 ± 0.5	10.9 ± 0.4	3.6 ± 0.1	2.0 ± 0.0	1.9 ± 0.2	–
D.I.U.2 (agg.)	1.0 ± 0.1	1.4 ± 0.3	82.1 ± 0.8	7.1 ± 0.4	5.2 ± 0.2	1.9 ± 0.2	1.3 ± 0.1	–
D.I.U.L	94.2 ± 1.0	1.0 ± 0.3	2.3 ± 0.5	1.7 ± 0.2	–	0.8 ± 0.1	–	–
D.Br	3.6 ± 0.7	2.6 ± 0.1	57.7 ± 0.2	19.1 ± 0.4	12.2 ± 0.6	2.0 ± 0.4	–	–

Samples collected from the halvet space



Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
D.H.D	42.1 ± 6.3	3.4 ± 0.2	33.7 ± 2.0	11.9 ± 2.5	4.7 ± 0.2	2.0 ± 0.5	2.2 ± 1.0	–
D.H.D (agg.)	1.6 ± 0.4	2.0 ± 0.2	69.7 ± 3.9	14.1 ± 1.8	6.9 ± 1.3	2.7 ± 0.5	3.2 ± 0.5	–
D.H.L.2	58.1 ±11.0	2.1 ± 0.3	24.3 ± 6.9	7.9 ± 1.8	3.0 ± 1.5	2.5 ± 0.6	2.2 ± 0.2	–
D.H.L.2 (agg.)	1.3 ± 0.1	1.9 ± 0.1	73.2 ± 0.8	12.2 ± 0.2	4.7 ± 2.1	3.1 ± 0.2	2.5 ± 0.0	–
D.H.U.2	47.5 ±11.1	2.1 ± 0.5	29.2 ± 7.5	12.7 ± 3.3	4.3 ± 0.7	1.5 ± 0.4	2.7 ± 0.5	–
D.H.U.2 (agg.)	1.4 ± 0.5	2.9 ± 0.1	59.0 ± 3.3	22.7 ± 2.7	8.3 ± 0.5	1.5 ± 0.1	4.2 ± 0.3	–
D.H.U.L	82.8 ± 5.3	1.6 ± 0.5	8.9 ± 5.7	2.1 ± 0.3	2.4 ± 0.3	1.6 ± 0.4	0.7 ± 0.3	–

Lime/aggregate ratios and lime percentages of plasters were also calculated by the results of EDS analyses. Lime percentage and lime/aggregate ratio values obtained from EDS analyses were nearly same with the results obtained from dissolving the binder in HCl (Table 4.4, Figure 4.4-4.6).

Table 4.4. Lime percentage and lime/aggregate values of plasters obtained by dissolving the binder in HCl and EDS analysis

	Dissolving the Binder in HCl		EDS Analysis	
	Lime %	Lime/Agg.	Lime %	Lime/Agg.
H.I.L	54.83	5/4	55.06	5/4
H.I.D.2	39.51	2/3	60.29	3/2
H.S.L	46.01	4/5	48.91	1/1
H.S.U.L	95.57	24/1	84.67	6/1
H.H.L	53.93	5/4	50.14	1/1
K.I.L	34.12	1/2	51.18	1/1
K.I.U.L	99.05	99/1	85.35	6/1
K.S.L.2	45.19	4/5	51.78	1/1
K.S.U.L	97.37	32/1	86.05	6/1
K.H.L.2	44.13	4/5	62.34	3/2
K.H.U.L	97.04	32/1	77.81	5/1
D.So.U.L.1	93.48	17/1	89.48	9/1
D.I.L	44.59	4/5	54.69	5/4
D.I.U.2	61.37	3/2	56.75	5/4
D.I.U.L	97.44	32/1	92.73	9/1
D.H.L.2	51.92	1/1	63.85	2/1
D.H.U.2	48.73	1/1	56.27	5/4
D.H.U.L	95.64	24/1	81.14	4/1
D.H.D	38.57	2/3	56.10	5/4

4.7. Hydraulicity of Plasters

Hydraulic properties of the plasters were determined by heating the plaster samples in a furnace at 200, 600 and 900 ºC. Weight losses at 200, 600 and 900ºC were mainly due to the loss of adsorbed water, chemically bound water, and the carbon dioxide respectively. If the ratio of CO_2/chemically bound water (H_2O) is between 1 and 10, the plasters can be accepted as hydraulic (Bakolas et. al. 1998, Moropoulou et. al. 2000a).

Horasan plaster samples had CO_2 and chemically bound water percents ranging between 9.76-28.92 % and 2.90-15.29 % respectively. The ratios of CO_2/H_2O were lower than 10, ranging between 0.64-9.01 (Table 4.5). Hence, all the horasan plaster samples could be regarded as hydraulic. Hydraulic character of horasan plasters could be attributed to the use of pozzolanic crushed brick aggregates

Table 4.5. Chemically bound water (H_2O), CO_2 percents and CO_2/H_2O ratios of horasan plasters

Sample	**H_2O (%)**	**CO_2 (%)**	**CO_2/H_2O**
H.I.D.2	3.66	17.05	4.66
H.I.L	15.29	9.76	0.64
H.S.L	6.02	17.52	2.91
H.H.L	6.41	14.42	2.25
K.I.L	4.96	14.60	2.95
K.S.L.2	10.57	11.87	1.12
K.H.L.2	2.90	24.33	8.39
D.I.L	3.21	28.92	9.01
D.I.U.2	6.40	20.52	3.21
D.H.L.2	5.64	20.47	3.63
D.H.U.2	4.29	23.85	5.55
D.H.D	6.20	15.68	2.53

Lime plaster samples had high percents of CO_2 and low percents of chemically bound water. CO_2 percents were in the range of 37.02-39.56 % and chemically bound water percents were 1.96-3.21 % (Table 4.5). The CO_2/H_2O ratios of lime plasters were over than 10. Thus, lime plasters could be regarded as non-hydraulic.

Table 4.6. Chemically bound water (H_2O), CO_2 percents and CO_2/H_2O ratios of lime plasters

Sample	**H_2O (%)**	**CO_2 (%)**	**CO_2/H_2O**
H.S.U.L	2.96	37.03	12.50
K.I.U.L	2.90	37.02	12.79
K.S.U.L	2.80	39.18	13.99
K.H.U.L	3.21	38.47	11.99
D.So.U.L.1	1.96	39.56	20.20
D.I.U.L	1.96	39.24	19.99
D.H.U.L	3.02	37.73	12.51

Hydraulicity levels of mortars and plasters are usually expressed by a graph on which the ratio of CO_2/chemically bound water versus CO_2 percent is given (Moropouolu et al. 2000a, Moropoulou et. al. 2000b, Moropoulou et. al. 2002a). When investigated horasan plasters and lime plasters were put on this graph, it was clearly observed that horasan plasters were concentrated at the bottom left part of the graph with their CO_2/H_2O ratio less than 10, and lime plasters were concentrated at the upper right part of the graph with their CO_2/H_2O ratio greater than 10 (Figure 4.54).

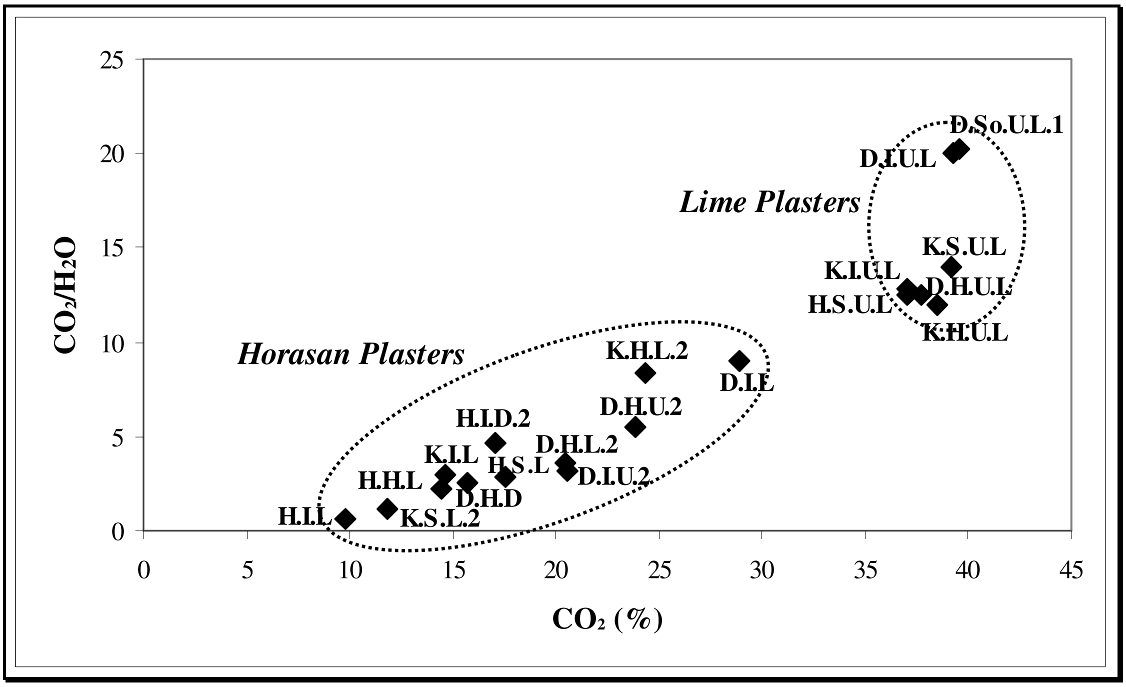


Figure 4.54. Hydraulicity (CO_2/H_2O) versus CO_2 % of plasters

CHAPTER 5

CONCLUSIONS

Characteristics of horasan and lime plasters, brick aggregates of horasan plasters and building bricks of three coeval Ottoman bath buildings in Urla and Seferihisar have been determined.

Two different plaster applications which can be distinguished with their texture and color are observed on the wall surfaces of the interior spaces of the baths. Lower levels which are extended to ~ 1.5 m. height above the existing floor surface are composed of one, two or three rough horasan plaster layers with a very thin finishing layer. However, upper levels are composed of a rough horasan plaster layer with a fine lime plaster layer.

Multi layered horasan plaster application with the less porous finishing layers provide a waterproof surface to lower levels which are subjected to water more than upper levels, and by this way prevent water entry into the structure

All horasan plasters used in different spaces, levels and layers have almost same physical properties, chemical and mineralogical compositions, microstructural and hydraulic properties.

Horasan plasters are porous and low dense materials. They are composed of lime and brick aggregates. Their lime/aggregate ratios are varied in the range of 1/2 and 3/2 by weight. Aggregates with particle sizes greater than 1180 µm. constitute the major fraction of total of the aggregates.

Less porous finishing layer which was applied on lower level horasan plasters is composed of fine brick powder and lime.

Lime plasters which were applied on upper level horasan plasters are composed of high amount of lime and a small amount of fine sand aggregates.

Crushed brick aggregates of all horasan plasters are good pozzolans since they were manufactured using high amounts of calcium-poor clays which were fired at low temperatures (< 900 °C) and they have high amounts of SiO_2 and low amounts of Fe_2O_3.

Bricks used in the domes of the baths were also produced from calcium-poor clays and fired at low temperatures. However, they are non-pozzolanic due to having lower amounts of clay minerals and higher amounts of Fe_2O_3 compared with brick aggregates.

This indicates that crushed brick aggregates were manufactured intentionally regarding their function in plasters.

All horasan plasters are hydraulic owing to the pozzolanic characteristics of crushed brick aggregates. However, lime plasters applied on upper level horasan plasters are non-hydraulic.

Horasan plasters are durable materials for the high humid and hot atmosphere of bath buildings. Their durability can be explained by their hydraulic characteristics, and the use of high porous brick aggregates which allows the calcite precipitation to be formed inside the pores.

This study showed that characterization of horasan plasters which were widely used in several historic buildings is important to determine the characteristics of new horasan plasters to be prepared for restorations.

New horasan plasters to be used in restoration of the baths must have the basic characteristics which were determined in this study.

Pure lime must be used in the manufacturing of intervention plasters. Brick aggregates must be high porous, must have a high amount of clay minerals and must be fired at low temperatures to provide good pozzolanicity. Brick aggregates and lime must be mixed well during their preparation to obtain durable plasters.

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APPENDIX A

BASIC PHYSICAL PROPERTIES OF PLASTERS

Table A.1. Density and porosity values of samples collected from Hersekzade Bath

Sample	Dry Weight (g)	Saturated Weight (g)	Archimedes Weight (g)	Density (g/cm^3)	Porosity (%)
H.I.L-1	6.76	10.14	3.92	1.09	54.34
H.I.L-2		11.28	4.37	1.26	37.34
H.I.L				**45.84**	**1.17**
H.I.U-1	9.44	14.99	5.49	0.99	58.42
H.I.U-2	3.85	6.03	2.21	1.01	57.07
H.I.U				**1.00**	**57.74**
H.I.D.1-1	51.42	70.15	30.64	1.30	47.41
H.I.D.1-2	49.50	66.15	29.68	1.36	45.65
H.I.D.1				**1.33**	**46.53**
H.I.D.2-1	42.32	53.87	25.89	1.51	41.28
H.I.D.2-2	35.25	44.37	21.49	1.54	39.06
H.I.D.2				**1.53**	**40.57**
H.S.L-1	31.65	42.44	19.10	1.36	46.23
H.S.L-2	29.04	38.76	17.15	1.34	44.98
H.S.L				**1.35**	**45.60**
H.S.U-1	17.56	22.52	10.69	1.48	41.93
H.S.U-2	21.42	27.30	12.86	1.48	40.72
H.S.U				**1.48**	**41.32**
H.S.U.L-1	3.57	4.57	2.00	1.39	38.91
H.S.U.L-2	4.46	5.86	2.51	1.33	41.79
H.S.U.L				**1.36**	**40.35**
H.H.L-1	10.77	14.05	6.36	1.40	42.65
H.H.L-2	8.58	11.40	5.01	1.34	44.13
H.H.L				**1.37**	**43.39**
H.H.U-1	26.65	38.73	15.90	52.91	1.17
H.H.U-2	9.22	13.04	5.39	49.93	1.21
H.H.U				**51.42**	**1.19**

Table A.2. Density and porosity values of samples collected from Kamanlı Bath

Sample	Dry Weight (g)	Saturated Weight (g)	Archimedes Weight (g)	Density (g/cm^3)	Porosity (%)
K.I.L-1	14.98	20.09	9.04	1.36	46.24
K.I.L-2	9.96	13.72	5.99	1.29	48.64
K.I.L				**1.32**	**47.44**
K.I.U-1	17.73	22.84	10.66	1.46	41.95
K.I.U-2	4.61	5.69	2.78	1.58	37.11
K.I.U				**1.52**	**39.53**
K.I.U.L-1	0.91	1.16	0.47	1.32	36.23
K.I.U.L-2	0.71	0.89	0.35	1.31	33.33
K.I.U.L				**1.32**	**34.78**
K.S.L.1-1	8.51	11.00	4.78	1.37	40.03
K.S.L.1-2	10.23	13.87	5.62	1.24	44.12
K.S.L.1				**1.30**	**42.08**
K.S.L.2-1	11.96	17.26	7.50	1.23	54.30
K.S.L.2-2	8.87	13.09	5.31	1.14	54.24
K.S.L.2				**1.18**	**54.27**
K.S.U-1	13.97	17.70	8.40	1.50	40.11
K.S.U-2	12.12	14.61	7.37	1.67	34.39
K.S.U				**1.59**	**37.25**
K.S.U.L-1	4.08	4.72	2.48	1.82	28.57
K.S.U.L-2	6.34	7.39	3.87	1.80	29.83
K.S.U.L				**1.81**	**29.20**
K.H.L.1-1	9.61	12.30	5.74	1.46	41.01
K.H.L.1-2	8.40	10.76	5.04	1.47	41.26
K.H.L.1				**1.47**	**41.13**
K.H.L.2-1	13.66	16.36	8.37	1.71	33.79
K.H.L.2-2	6.58	7.77	4.03	1.76	31.82
K.H.L.2				**1.73**	**32.81**
K.H.L.3-1	9.48	12.28	5.69	1.44	42.49
K.H.L.3-2	17.30	21.88	10.33	1.50	39.65
K.H.L.3				**1.47**	**41.07**
K.H.U-1	5.89	7.63	3.53	1.44	42.44
K.H.U-2	9.18	11.88	5.49	1.44	42.25
K.H.U				**1.44**	**42.35**
K.H.U.L-1	7.57	10.02	4.62	1.40	45.37
K.H.U.L-2	8.41	11.24	5.05	1.36	45.72
K.H.U.L				**1.38**	**45.54**

Table A.3. Density and porosity values of samples collected from Düzce Bath

Sample	Dry Weight (g)	Saturated Weight (g)	Archimedes Weight (g)	Density (g/cm^3)	Porosity (%)
D.So.L.1-1	13.12	16.69	7.77	1.47	40.02
D.So.L.1-2	15.71	19.52	9.13	1.51	36.67
D.So.L.1				**1.49**	**38.35**
D.So.L.2-1	24.75	29.57	14.61	1.65	32.22
D.So.L.2-2	25.94	30.71	15.19	1.67	30.73
D.So.L.2				**1.66**	**31.48**
D.So.U.L.1-1	3.28	3.78	1.82	1.67	25.51
D.So.U.L.1-2	4.41	4.99	2.53	1.79	23.58
D.So.U.L.1				**1.73**	**24.54**
D.So.U.L.2-1	4.81	6.34	2.70	1.32	42.03
D.So.U.L.2-2	2.53	3.34	1.29	1.23	39.51
D.So.U.L.2				**1.28**	**40.77**
D.I.L-1	14.87	19.56	8.79	1.38	43.55
D.I.L-2	16.84	21.79	9.92	1.42	41.70
D.I.L				**1.40**	**42.62**
D.I.U.1-1	12.24	16.43	7.95	1.44	49.41
D.I.U.1-2	13.56	17.62	9.12	1.60	47.76
D.I.U.1				**1.52**	**48.59**
D.I.U.2-1	7.59	10.56	4.93	1.35	52.75
D.I.U.2-2	4.51	5.83	2.77	1.47	43.14
D.I.U.2				**1.41**	**47.95**
D.I.U.L-1	1.56	1.96	1.02	1.66	42.55
D.I.U.L-2	1.56	2.03	0.86	1.33	40.17
D.I.U.L				**1.50**	**41.36**
D.H.L.1-1	19.61	26.03	11.75	1.37	44.96
D.H.L.1-2	13.08	17.40	7.65	1.34	44.31
D.H.L.1				**1.36**	**44.63**
D.H.L.2-1	14.84	18.24	8.97	1.60	36.68
D.H.L.2-2	7.53	9.17	4.49	1.61	35.04
D.H.L.2				**1.60**	**35.86**
D.H.L.3-1	12.61	15.53	7.22	1.52	35.14
D.H.L.3-2	11.29	13.50	6.16	1.54	30.11
D.H.L.3				**1.53**	**32.62**
D.H.U.1-1	30.12	38.77	20.26	1.63	46.73
D.H.U.1-2	33.89	43.75	18.00	1.32	38.29
D.H.U.1				**1.47**	**42.51**
D.H.U.2-1	9.70	12.20	5.65	1.48	38.17
D.H.U.2-2	25.26	32.83	15.33	1.44	43.26
D.H.U.2				**1.46**	**40.71**
D.H.U.L-1	1.34	1.62	0.83	1.70	35.44
D.H.U.L-2	1.36	1.76	0.74	1.33	39.22
D.H.U.L				**1.51**	**37.33**
D.H.D-1	14.53	18.12	8.55	1.52	37.51
D.H.D-2	12.71	15.77	7.41	1.52	36.60
D.H.D				**1.52**	**37.06**

APPENDIX B

LIME/AGGREGATE RATIOS OF PLASTERS AND PARTICLE SIZE DISTRIBUTIONS OF AGGREGATES

Table B.1. Lime/aggregate ratios and particle size distributions of aggregates of plaster samples collected from Hersekzade Bath

Sample	Lime (%)	Aggregate (%)	Aggregate Size Distribution (%)					
			≥1180 µm	500 µm	250 µm	125 µm	53 µm	<53 µm
H.I.L-1	54.98	45.02	13.46	12.33	7.29	6.89	3.13	1.17
H.I.L-2	54.69	45.31	16.08	12.49	7.68	6.16	1.91	0.47
H.I.L	**54.83**	**45.17**	**14.77**	**12.41**	**7.48**	**6.52**	**2.52**	**0.82**
H.I.U-1	43.50	56.50	26.75	14.81	6.50	4.38	2.77	0.53
H.I.U-2	44.47	55.53	31.46	12.68	5.24	3.03	2.24	0.19
H.I.U	**43.98**	**56.02**	**29.10**	**13.75**	**5.87**	**3.71**	**2.51**	**0.36**
H.I.D.1-1	53.66	46.34	23.93	11.42	5.19	3.31	1.42	0.71
H.I.D.1-2	49.56	50.44	25.82	12.13	5.80	3.95	1.83	0.54
H.I.D.1	**51.61**	**48.39**	**24.88**	**11.77**	**5.50**	**3.63**	**1.62**	**0.63**
H.I.D.2-1	41.76	58.24	29.87	10.98	6.15	4.72	4.58	1.42
H.I.D.2-2	37.25	62.75	36.72	10.32	5.99	4.33	3.76	1.04
H.I.D.2	**39.51**	**60.49**	**33.29**	**10.65**	**6.07**	**4.53**	**4.17**	**1.23**
H.S.L-1	46.96	53.04	22.36	12.77	6.91	5.33	4.04	1.23
H.S.L-2	45.07	54.93	21.45	13.15	9.02	6.42	3.66	0.72
H.S.L	**46.01**	**53.99**	**21.91**	**12.96**	**7.97**	**5.87**	**3.85**	**0.98**
H.S.U-1	51.95	48.05	19.50	9.30	6.74	6.05	4.65	1.60
H.S.U-2	54.13	45.87	18.40	10.07	6.51	5.42	3.98	1.19
H.S.U	**53.04**	**46.96**	**18.95**	**9.68**	**6.63**	**5.73**	**4.32**	**1.40**
H.S.U.L-1	95.32	4.68	0.31	0.50	0.92	1.34	0.73	3.36
H.S.U.L-2	95.81	4.19	0.00	0.00	0.00	0.00	0.00	0.61
H.S.U.L	**95.57**	**4.43**	**0.16**	**0.25**	**0.46**	**0.67**	**0.37**	**1.99**
H.H.L-1	61.62	38.38	11.77	10.48	6.45	4.48	3.66	0.58
H.H.L-2	46.23	53.77	24.48	14.09	6.25	4.09	3.25	0.61
H.H.L	**53.93**	**46.07**	**18.13**	**12.29**	**6.35**	**4.29**	**3.46**	**0.59**
H.H.U-1	48.28	51.72	19.56	13.97	9.18	6.96	1.63	0.25
H.H.U-2	55.43	44.57	18.21	13.52	6.14	3.38	2.07	0.98
H.H.U	**51.85**	**48.15**	**18.88**	**13.74**	**7.66**	**5.17**	**1.85**	**0.61**

Table B.2. Lime/aggregate ratios and particle size distributions of aggregates of plaster samples collected from Kamanlı Bath

Sample	Lime (%)	Aggregate (%)	Aggregate Size Distribution (%)					
			≥1180 μm	500 μm	250 μm	125 μm	53 μm	<53 μm
K.I.L-1	35.31	64.69	25.13	17.37	9.84	6.51	4.29	1.28
K.I.L-2	32.93	67.07	24.09	18.14	10.75	7.14	5.10	1.51
K.I.L	**34.12**	**65.88**	**24.61**	**17.75**	**10.30**	**6.83**	**4.69**	**1.39**
K.I.U-1	54.22	45.78	7.37	12.11	10.54	7.98	5.40	2.18
K.I.U-2	32.52	67.48	20.63	20.41	11.46	7.58	5.07	2.12
K.I.U	**43.37**	**56.63**	**14.00**	**16.26**	**11.00**	**7.78**	**5.24**	**2.15**
K.I.U.L-1	99.46	0.54	0.00	0.00	0.08	0.06	0.06	0.49
K.I.U.L-2	98.64	1.36	0.00	0.00	0.00	0.00	0.00	1.36
K.I.U.L	**99.05**	**0.95**	**0.00**	**0.00**	**0.04**	**0.03**	**0.03**	**0.93**
K.S.L.1-1	50.79	49.21	10.22	17.12	8.73	5.59	4.75	2.29
K.S.L.1-2	61.66	38.34	9.06	10.21	7.01	5.25	4.21	1.74
K.S.L.1	**56.23**	**43.77**	**9.64**	**13.66**	**7.87**	**5.42**	**4.48**	**2.02**
K.S.L.2-1	39.54	60.46	18.92	18.10	10.54	6.72	4.49	1.29
K.S.L.2-2	50.84	49.16	6.81	16.86	10.03	7.06	5.93	1.86
K.S.L.2	**45.19**	**54.81**	**12.87**	**17.48**	**10.29**	**6.89**	**5.21**	**1.58**
K.S.U-1	45.69	54.31	24.31	11.97	6.54	5.66	4.38	0.93
K.S.U-2	47.36	52.64	24.22	11.23	6.39	6.07	3.52	0.85
K.S.U	**46.53**	**53.47**	**24.26**	**11.60**	**6.47**	**5.87**	**3.95**	**0.89**
K.S.U.L-1	96.75	3.25	0.00	0.19	0.46	0.60	0.32	1.64
K.S.U.L-2	97.99	2.01	0.00	0.00	0.00	0.00	0.00	2.24
K.S.U.L	**97.37**	**2.63**	**0.00**	**0.10**	**0.23**	**0.30**	**0.16**	**1.94**
K.H.L.1-1	44.78	55.22	21.83	10.98	8.76	6.38	5.09	1.70
K.H.L.1-2	43.47	56.53	24.61	11.12	7.98	5.88	4.68	1.83
K.H.L.1	**44.13**	**55.87**	**23.22**	**11.05**	**8.37**	**6.13**	**4.89**	**1.77**
K.H.L.2-1	54.62	45.38	16.92	10.30	7.14	5.17	3.17	2.36
K.H.L.2-2	54.56	45.44	18.88	8.04	6.62	5.45	3.56	2.30
K.H.L.2	**54.59**	**45.41**	**17.90**	**9.17**	**6.88**	**5.31**	**3.36**	**2.33**
K.H.L.3-1	42.03	57.97	22.41	14.60	8.26	5.60	4.98	1.41
K.H.L.3-2	43.09	56.91	25.92	14.16	7.33	4.64	3.00	1.18
K.H.L.3	**42.56**	**57.44**	**24.16**	**14.38**	**7.80**	**5.12**	**3.99**	**1.29**
K.H.U-1	45.81	54.19	17.68	13.93	9.18	6.46	4.76	1.42
K.H.U-2	53.76	46.24	9.98	12.09	9.04	7.31	4.60	2.31
K.H.U	**49.78**	**50.22**	**13.83**	**13.01**	**9.11**	**6.88**	**4.68**	**1.86**
K.H.U.L-1	97.87	2.13	0.01	0.19	0.45	0.44	0.27	0.55
K.H.U.L-2	96.21	3.79	0.05	0.78	0.86	0.62	0.27	1.12
K.H.U.L	**97.04**	**2.96**	**0.03**	**0.49**	**0.65**	**0.53**	**0.27**	**0.84**

Table B.3. Lime/aggregate ratios and particle size distributions of aggregates of plaster samples collected from Düzce Bath

Sample	Lime (%)	Aggregate (%)	Aggregate Size Distribution (%)					
			≥1180 µm	500 µm	250 µm	125 µm	53 µm	<53 µm
D.So.L.1-1	60.71	39.29	9.12	6.40	4.97	6.84	6.94	4.69
D.So.L.1-2	57.62	42.38	10.70	6.77	5.28	6.01	7.18	5.97
D.So.L.1	**59.17**	**40.83**	**9.91**	**6.58**	**5.13**	**6.43**	**7.06**	**5.33**
D.So.L.2-1	47.84	52.16	17.45	7.64	5.59	6.34	8.26	6.51
D.So.L.2-2	54.04	45.96	12.37	7.89	5.65	7.62	6.63	5.45
D.So.L.2	**50.94**	**49.06**	**14.91**	**7.76**	**5.62**	**6.98**	**7.44**	**5.98**
D.So.U.L.1-1	94.71	5.29	0.00	0.21	0.18	0.08	0.08	4.10
D.So.U.L.1-2	92.25	7.75	0.00	1.58	1.55	0.16	0.12	4.97
D.So.U.L.1	**93.48**	**6.52**	**0.00**	**0.90**	**0.87**	**0.12**	**0.10**	**4.54**
D.So.U.L.2-1	91.94	8.06	0.21	0.19	0.24	6.45	0.25	0.41
D.So.U.L.2-2	94.19	5.81	0.03	3.43	0.25	0.31	0.30	4.57
D.So.U.L.2	**93.06**	**6.94**	**0.12**	**1.81**	**0.24**	**3.38**	**0.27**	**2.49**
D.I.L-1	42.22	57.78	30.66	12.18	6.19	4.17	2.72	1.51
D.I.L-2	46.97	53.03	25.24	12.84	6.35	4.02	2.76	1.55
D.I.L	**44.59**	**55.41**	**27.95**	**12.51**	**6.27**	**4.09**	**2.74**	**1.53**
D.I.U.1-1	59.05	40.95	14.99	9.13	6.12	4.67	3.60	2.34
D.I.U.1-2	59.42	40.58	14.89	8.31	5.38	4.70	4.25	3.01
D.I.U.1	**59.23**	**40.77**	**14.94**	**8.72**	**5.75**	**4.68**	**3.93**	**2.67**
D.I.U.2-1	66.66	33.34	11.74	8.56	5.44	3.61	2.53	1.22
D.I.U.2-2	56.09	43.91	16.65	10.59	6.73	4.60	3.36	1.95
D.I.U.2	**61.37**	**38.63**	**14.20**	**9.57**	**6.09**	**4.10**	**2.95**	**1.58**
D.I.U.L-1	97.65	2.35	0.00	0.03	0.08	0.09	0.06	3.16
D.I.U.L-2	97.23	2.77	0.00	0.12	0.09	0.06	0.01	2.64
D.I.U.L	**97.44**	**2.56**	**0.00**	**0.08**	**0.08**	**0.07**	**0.03**	**2.90**
D.H.L.1-1	50.66	49.34	15.73	15.11	8.32	5.24	2.94	2.04
D.H.L.1-2	53.07	46.93	11.07	9.39	8.68	9.86	5.28	2.66
D.H.L.1	**51.87**	**48.13**	**13.40**	**12.25**	**8.50**	**7.55**	**4.11**	**2.35**
D.H.L.2-1	50.62	49.38	21.87	10.96	7.74	5.63	2.36	0.94
D.H.L.2-2	53.21	46.79	18.91	10.98	6.39	4.82	3.78	1.74
D.H.L.2	**51.92**	**48.08**	**20.39**	**10.97**	**7.07**	**5.22**	**3.07**	**1.34**
D.H.L.3-1	59.24	40.76	16.29	11.04	6.44	4.11	1.81	1.31
D.H.L.3-2	54.50	45.50	15.80	10.53	8.02	6.28	3.00	1.62
D.H.L.3	**56.87**	**43.13**	**16.05**	**10.78**	**7.23**	**5.20**	**2.41**	**1.46**
D.H.U.1-1	39.24	60.76	27.91	13.39	9.17	6.03	3.02	1.41
D.H.U.1-2	39.42	60.58	29.13	13.06	8.67	5.21	3.12	1.57
D.H.U.1	**39.33**	**60.67**	**28.52**	**13.23**	**8.92**	**5.62**	**3.07**	**1.49**
D.H.U.2-1	51.68	48.32	25.66	7.74	5.41	4.19	2.76	1.93
D.H.U.2-2	45.78	54.22	21.18	14.40	6.40	4.10	2.61	1.60
D.H.U.2	**48.73**	**51.27**	**23.42**	**11.07**	**5.91**	**4.14**	**2.68**	**1.76**
D.H.U.L-1	96.99	3.01	0.00	0.09	0.14	0.11	0.04	2.55
D.H.U.L-2	94.29	5.71	0.32	0.35	0.34	0.24	0.17	3.98
D.H.U.L	**95.64**	**4.36**	**0.16**	**0.22**	**0.24**	**0.18**	**0.10**	**3.27**
D.H.D-1	38.47	61.53	25.88	16.21	9.20	5.19	3.15	1.70
D.H.D-2	38.67	61.33	23.33	16.15	9.73	5.77	3.64	2.27
D.H.D	**38.57**	**61.43**	**24.60**	**16.18**	**9.47**	**5.48**	**3.40**	**1.98**

APPENDIX C

POZZOLANIC ACTIVITY OF BRICK AGGREGATES AND BUILDING BRICKS DETERMINED BY ELECTRICAL CONDUCTIVITY METHOD

Table C.1. Pozzolanic activity of brick aggregates used in horasan plasters by electrical conductivity method

Sample	Electrical conductivity of $Ca(OH)_2$ (mS/cm)	Electrical conductivity of $Ca(OH)_2$ after addition of brick powders (mS/cm)	Difference in conductivity
H.I.L	8.16	1.51	6.65
H.I.D.2	8.14	3.81	4.33
H.S.L	8.23	2.30	5.93
H.H.L	8.13	0.79	7.34
K.I.L	8.18	1.72	6.46
K.S.L.2	8.12	2.31	5.81
K.H.L.2	8.19	6.61	1.58
D.I.L	8.16	0.88	7.28
D.I.U.2	8.18	0.36	7.82
D.H.L.2	8.25	5.18	3.07
D.H.U.2	8.18	4.92	3.26
D.H.D	8.24	3.18	5.06

Table C.2. Pozzolanic activity of building bricks by electrical conductivity method

Sample	Electrical conductivity of $Ca(OH)_2$ (mS/cm)	Electrical conductivity of $Ca(OH)_2$ after addition of brick powders (mS/cm)	Difference in conductivity
H.Br	8.20	7.98	0.22
K.Br	8.18	7.72	0.46
D.Br	8.18	7.51	0.67

APPENDIX D

POZZOLANIC ACTIVITY OF BRICK AGGREGATES AND BUILDING BRICKS DETERMINED BY MEASURING AMOUNT CALCIUM IONS REACTED WITH BRICK POWDERS

Table D.1. Amount of lime reacted with brick aggregate powders after 8, 16 and 30 days

Sample	Amount of lime reacted with brick powders after 8 days (g)	Amount of lime reacted with brick powders after 16 days (g)	Amount of lime reacted with brick powders after 30 days (g)
H.I.L	0.23	1.59	9.71
H.I.D.2	2.06	5.86	17.52
H.S.L	0.19	1.70	8.15
H.H.L	0.23	1.54	6.46
K.I.L	0.66	2.08	10.07
K.S.L.2	1.25	7.30	14.11
K.H.L.2	3.50	12.48	23.43
D.I.L	0.28	2.70	9.16
D.I.U.2	0.40	2.05	7.33
D.H.L.2	1.89	5.00	17.25
D.H.U.2	3.80	9.41	21.90
D.H.D	5.49	10.94	19.17

Table D.2. Amount of lime reacted with building brick powders after 8, 16 and 30 days

Sample	Amount of lime reacted with brick powders after 8 days (g)	Amount of lime reacted with brick powders after 16 days (g)	Amount of lime reacted with brick powders after 30 days (g)
H.Br	3.33	9.27	21.17
K.Br	3.54	11.75	21.39
D.Br	3.16	11.97	23.39

Table D.3. Amount sodium oxide (Na_2O) in calcium hydroxide solution mixed with crushed bricks after 8, 16 and 30 days

Sample	Amount of sodium oxide after 8 days (mg)	Amount of sodium oxide after 16 days (mg)	Amount of sodium oxide after 30 days (mg)
H.I.L	0.23	1.59	9.71
H.I.D.2	2.06	5.86	17.52
H.S.L	0.19	1.70	8.15
H.H.L	0.23	1.54	6.46
K.I.L	0.66	2.08	10.07
K.S.L.2	1.25	7.30	14.11
K.H.L.2	3.50	12.48	23.43
D.I.L	0.28	2.70	9.16
D.I.U.2	0.40	2.05	7.33
D.H.L.2	1.89	5.00	17.25
D.H.U.2	3.80	9.41	21.90
D.H.D	5.49	10.94	19.17

Table D.4. Amount sodium oxide (Na_2O) in calcium hydroxide solution mixed with building bricks after 8, 16 and 30 days

Sample	Amount of sodium oxide after 8 days (mg)	Amount of sodium oxide after 16 days (mg)	Amount of sodium oxide after 30 days (mg)
H.Br	3.33	9.27	21.17
K.Br	3.54	11.75	21.39
D.Br	3.16	11.97	23.39

Table D.5. Amount potassium oxide (K_2O) in calcium hydroxide solution mixed with crushed bricks after 8, 16 and 30 days

Sample	Amount of potassium oxide after 8 days (mg)	Amount of potassium oxide after 16 days (mg)	Amount of potassium oxide after 30 days (mg)
H.I.L	0.00	0.68	3.58
H.I.D.2	1.28	10.24	18.01
H.S.L	0.00	1.35	4.33
H.H.L	0.00	0.35	2.41
K.I.L	0.27	1.42	4.07
K.S.L.2	0.48	6.90	12.16
K.H.L.2	3.33	3.92	12.26
D.I.L	0.00	1.18	3.99
D.I.U.2	0.00	0.39	2.28
D.H.L.2	1.91	5.54	11.13
D.H.U.2	6.84	28.05	45.08
D.H.D	2.42	8.40	12.81

Table D.6. Amount potassium oxide (K_2O) in calcium hydroxide solution mixed with building bricks after 8, 16 and 30 days

Sample	Amount of potassium oxide after 8 days (mg)	Amount of potassium oxide after 16 days (mg)	Amount of potassium oxide after 30 days (mg)
H.Br	3.88	19.58	33.52
K.Br	6.24	24.58	41.60
D.Br	2.36	14.74	26.16

APPENDIX E

CHEMICAL COMPOSITIONS OF PLASTERS, BRICK AGGREGATES AND BUILDING BRICKS

Table E.1. Chemical compositions of plasters, brick aggregates and building brick collected from Hersekzade Bath

Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
H.I.L-1	41.13	4.44	28.48	11.20	2.81	2.85	1.12	7.96
H.I.L-2	39.33	4.87	28.02	11.15	2.88	3.78	1.18	8.78
H.I.L-3	38.47	5.26	28.26	11.50	3.33	3.86	1.09	8.24
H.I.L	**39.64**	**4.86**	**28.25**	**11.28**	**3.01**	**3.50**	**1.13**	**8.33**
H.I.L (agg.)-1	0.83	-	92.55	4.46	-	1.37	0.80	-
H.I.L (agg.)-2	1.64	-	91.84	4.64	-	1.04	0.84	-
H.I.L (agg.)-3	0.94	-	93.44	3.63	-	1.20	0.79	-
H.I.L (agg.)	**1.14**	**-**	**92.61**	**4.24**	**-**	**1.20**	**0.81**	**-**
H.I.D.2-1	50.77	1.94	28.36	10.53	4.36	1.61	2.07	0.37
H.I.D.2-2	51.94	1.94	26.33	10.17	4.42	1.86	2.33	1.02
H.I.D.2-3	50.84	2.00	26.78	10.33	5.36	2.07	1.96	0.66
H.I.D.2	**51.18**	**1.96**	**27.16**	**10.34**	**4.71**	**1.85**	**2.12**	0.68
H.I.D.2 (agg)-1	1.72	1.28	77.98	9.84	4.80	1.90	2.48	-
H.I.D.2 (agg)-2	1.40	1.70	77.83	10.12	4.21	2.45	2.28	-
H.I.D.2 (agg)-3	1.01	1.04	78.89	10.37	4.50	1.58	2.61	-
H.I.D.2 (agg.)	**1.38**	**1.34**	**78.23**	**10.11**	**4.50**	**1.98**	**2.46**	**-**
H.S.L-1	22.40	4.39	52.40	13.64	3.57	1.76	1.85	0.00
H.S.L-2	22.27	4.89	50.28	13.67	3.40	2.05	1.72	1.73
H.S.L-3	23.43	4.97	50.00	13.17	2.86	1.98	1.78	1.81
H.S.L	**22.70**	**4.75**	**50.89**	**13.49**	**3.28**	**1.93**	**1.78**	**1.18**
H.S.L (agg.)-1	1.11	1.11	80.56	8.94	3.21	2.78	2.29	-
H.S.L (agg.)-2	1.18	0.78	80.75	9.07	3.94	2.28	2.01	-
H.S.L (agg.)-3	0.97	0.81	82.74	8.45	3.14	1.96	1.93	-
H.S.L (agg.)	**1.09**	**0.90**	**81.35**	**8.82**	**3.43**	**2.34**	**2.08**	**-**
H.S.U.L-1	87.22	1.80	6.59	2.06	-	0.67	-	1.67
H.S.U.L-2	85.92	2.09	7.04	2.31	-	0.56	-	2.08
H.S.U.L-3	86.62	1.79	7.06	2.07	-	0.90	-	1.57
H.S.U.L	**86.59**	**1.89**	**6.90**	**2.15**	**-**	**0.71**	**-**	**1.77**
H.H.L-1	25.96	2.95	44.56	17.02	4.06	3.08	1.65	0.72
H.H.L-2	26.55	3.21	43.13	16.30	4.46	2.81	1.52	2.03
H.H.L-3	26.81	2.85	43.84	16.60	3.67	2.84	1.51	1.89
H.H.L	**26.44**	**3.00**	**43.84**	**16.64**	**4.06**	**2.91**	**1.56**	**1.55**
H.H.L (agg.)-1	0.80	0.00	88.29	5.88	2.08	1.94	1.01	-
H.H.L (agg.)-2	0.99	1.07	86.71	5.96	2.24	2.10	0.93	-
H.H.L (agg.)-3	0.74	0.81	87.68	5.47	2.50	1.60	1.19	-
H.H.L (agg.)	**0.84**	**0.63**	**87.56**	**5.77**	**2.27**	**1.88**	**1.04**	**-**
H.Br-1	1.57	3.11	55.60	24.07	8.66	2.01	3.38	1.60
H.Br-2	1.27	3.01	54.97	23.74	9.80	2.05	3.51	1.66
H.Br-3	2.08	2.90	54.25	24.08	9.30	1.84	3.59	1.96
H.Br	**1.64**	**3.01**	**54.94**	**23.96**	**9.25**	**1.97**	**3.49**	**1.74**

Table E.2. Chemical compositions of plasters, brick aggregates and building brick collected from Kamanlı Bath

Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
K.I.L-1	29.50	2.89	43.54	13.80	4.74	2.55	2.43	0.55
K.I.L-2	29.85	2.71	43.27	13.44	5.39	2.49	2.41	0.43
K.I.L-3	28.85	2.93	43.89	13.91	4.78	2.34	2.71	0.59
K.I.L	**29.40**	**2.84**	**43.57**	**13.72**	**4.97**	**2.46**	**2.52**	**0.52**
K.I.L (agg.)-1	1.11	1.49	77.83	9.87	4.97	2.99	1.75	-
K.I.L (agg.)-2	1.29	2.13	76.72	10.15	5.12	2.72	1.87	-
K.I.L (agg.)-3	1.23	1.62	77.30	9.93	5.85	2.13	1.94	-
K.I.L (agg.)	**1.21**	**1.75**	**77.28**	**9.98**	**5.31**	**2.61**	**1.85**	**-**
K.I.U.L-1	89.12	1.50	3.44	1.94	-	1.02	-	2.98
K.I.U.L-2	86.35	2.14	3.29	2.40	-	1.66	-	4.17
K.I.U.L-3	86.51	1.54	3.30	3.04	-	1.78	-	3.82
K.I.U.L	**87.33**	**1.73**	**3.34**	**2.46**	**-**	**1.49**	**-**	**3.66**
K.S.L.2-1	32.04	2.66	40.82	14.09	4.35	2.74	1.60	1.70
K.S.L.2-2	29.55	2.63	41.72	13.83	6.17	2.84	1.72	1.53
K.S.L.2-3	31.70	2.11	41.95	13.07	5.19	2.16	1.70	2.11
K.S.L.2	**31.10**	**2.47**	**41.50**	**13.66**	**5.24**	**2.58**	**1.67**	**1.78**
K.S.L.2 (agg)-1	1.36	1.60	84.93	6.35	3.35	1.56	0.84	-
K.S.L.2 (agg)-2	1.42	1.78	83.23	6.97	3.90	1.70	0.99	-
K.S.L.2 (agg)-3	1.59	1.77	82.13	6.96	4.92	1.54	1.09	-
K.S.L.2(agg.)	**1.46**	**1.72**	**83.43**	**6.76**	**4.06**	**1.60**	**0.97**	**-**
K.S.U.L-1	88.89	4.23	4.68	2.20	-	-	-	-
K.S.U.L-2	88.89	4.00	4.54	2.47	-	-	-	-
K.S.U.L-3	86.26	4.63	5.68	3.41	-	-	-	-
K.S.U.L	**88.01**	**4.29**	**4.97**	**2.69**	**-**	**-**	**-**	**-**
K.H.L.2-1	55.15	2.77	24.91	8.70	3.49	2.49	1.83	0.65
K.H.L.2-2	54.31	2.68	25.19	8.63	4.07	2.60	1.90	0.62
K.H.L.2-3	56.37	2.41	24.62	8.58	3.42	2.40	1.88	0.32
K.H.L.2	**55.28**	**2.62**	**24.91**	**8.64**	**3.66**	**2.50**	**1.87**	**0.53**
K.H.L.2(agg)-1	1.57	1.86	68.41	14.28	7.26	3.51	3.11	-
K.H.L.2(agg)-2	2.06	1.88	67.88	14.29	7.32	3.55	3.02	-
K.H.L.2(agg)-3	1.55	1.59	69.26	14.03	6.90	3.42	3.26	-
K.H.L.2(agg.)	**1.73**	**1.78**	**68.52**	**14.20**	**7.16**	**3.49**	**3.13**	**-**
K.H.U.L-1	79.61	3.49	4.51	3.28	2.41	2.38	0.95	3.36
K.H.U.L-2	79.51	3.70	4.41	3.58	2.01	2.37	1.22	3.20
K.H.U.L-3	77.58	3.84	4.11	3.41	3.86	2.01	1.30	3.90
K.H.U.L	**78.90**	**3.68**	**4.34**	**3.42**	**2.76**	**2.25**	**1.16**	3.49
K.Br-1	3.47	2.46	59.30	20.32	9.18	1.84	3.47	-
K.Br-2	3.79	2.66	58.61	20.67	8.11	2.15	3.79	-
K.Br-3	3.74	2.69	59.82	19.85	8.39	1.97	3.74	-
K.Br	**3.67**	**2.60**	**59.24**	**20.28**	**8.56**	**1.99**	**3.67**	**-**

Table E.3. Chemical compositions of plasters, brick aggregates and building brick collected from Düzce Bath

Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Other
D.So.U.L.1-1	92.49	1.52	3.22	1.36	-	1.52	-	-
D.So.U.L.1-2	90.48	1.85	3.49	2.46	-	1.85	-	-
D.So.U.L.1-3	91.07	1.75	3.01	2.13	-	1.75	-	-
D.So.U.L.1	**91.35**	**1.71**	**3.24**	**1.98**	**-**	**1.71**	**-**	**-**
D.I.L-1	39.96	2.77	36.97	11.92	4.01	1.95	2.42	-
D.I.L-2	38.03	2.76	38.42	11.76	4.18	2.32	2.54	-
D.I.L-3	38.08	3.02	39.27	11.59	3.88	2.13	2.03	-
D.I.L	**38.69**	**2.85**	**38.22**	**11.76**	**4.02**	**2.13**	**2.33**	**-**
D.I.L (agg.)-1	1.61	1.71	81.23	7.96	4.06	2.07	1.36	-
D.I.L (agg.)-2	1.63	1.41	80.96	7.57	4.94	1.85	1.64	-
D.I.L (agg.)-3	1.69	1.29	80.45	8.07	5.06	1.62	1.83	-
D.I.L (agg.)	**1.64**	**1.47**	**80.88**	**7.87**	**4.69**	**1.85**	**1.61**	**-**
D.I.U.2-1	43.44	2.21	36.50	10.63	3.52	2.02	1.68	-
D.I.U.2-2	43.50	1.63	36.30	10.77	3.78	2.02	2.01	-
D.I.U.2-3	43.92	1.83	35.59	11.33	3.51	1.96	1.86	-
D.I.U.2	**43.62**	**1.89**	**36.13**	**10.91**	**3.60**	**2.00**	**1.85**	**-**
D.I.U.2 (agg)-1	0.96	1.48	82.43	6.87	5.02	1.92	1.31	-
D.I.U.2 (agg)-2	1.06	1.54	81.21	7.58	5.33	2.01	1.28	-
D.I.U.2 (agg)-3	0.98	1.05	82.75	6.98	5.21	1.67	1.37	-
D.I.U.2 (agg.)	**1.00**	**1.36**	**82.13**	**7.14**	**5.19**	**1.87**	**1.32**	**-**
D.I.U.L-1	94.25	1.21	2.06	1.58	-	0.91	-	-
D.I.U.L-2	95.13	0.66	1.99	1.45	-	0.77	-	-
D.I.U.L-3	93.19	1.26	2.88	1.91	-	0.75	-	-
D.I.U.L	**94.19**	**1.04**	**2.31**	**1.65**	**-**	**0.81**	**-**	**-**
D.H.L.2-1	67.99	1.81	17.96	6.24	2.10	1.94	1.96	-
D.H.L.2-2	46.19	2.20	31.59	9.85	4.76	3.10	2.32	-
D.H.L.2-3	60.13	2.40	23.19	7.48	2.27	2.33	2.20	-
D.H.L.2	**58.10**	**2.14**	**24.25**	**7.86**	**3.04**	**2.46**	**2.16**	**-**
D.H.L.2(agg)-1	1.20	1.86	74.09	11.92	2.33	2.79	2.47	-
D.H.L.2(agg)-2	1.34	1.86	73.15	12.31	5.76	3.14	2.44	-
D.H.L.2(agg)-3	1.47	2.02	72.41	12.26	6.12	3.22	2.49	-
D.H.L.2 (agg)	**1.34**	**1.91**	**73.22**	**12.16**	**4.74**	**3.05**	**2.47**	**-**
D.H.U.2-1	46.49	2.66	26.65	15.17	4.41	2.05	2.57	-
D.H.U.2-2	40.83	1.75	33.17	14.88	4.82	1.23	3.32	-
D.H.U.2-3	39.06	2.42	37.07	12.43	4.71	1.51	2.79	-
D.H.U.2-4	63.50	1.72	19.95	8.11	3.25	1.23	2.22	-
D.H.U.2	**47.47**	**2.14**	**29.21**	**12.65**	**4.30**	**1.51**	**2.73**	**-**
D.H.U.2(agg)-1	1.89	2.94	60.30	20.90	8.64	1.52	3.81	-
D.H.U.2(agg)-2	1.50	2.95	55.22	25.81	8.47	1.64	4.41	-
D.H.U.2(agg)-3	0.88	2.75	61.45	21.53	7.65	1.41	4.34	-
D.H.U.2 (agg)	**1.42**	**2.88**	**58.99**	**22.75**	**8.25**	**1.52**	**4.19**	**-**
D.H.U.L-1	76.83	1.52	14.83	1.83	2.43	1.51	1.04	-
D.H.U.L-2	84.77	1.13	8.27	2.03	2.07	1.20	0.53	-
D.H.U.L-3	86.89	2.02	3.45	2.33	2.70	1.97	0.64	-
D.H.U.L	**82.83**	**1.56**	**8.85**	**2.06**	**2.40**	**1.56**	**0.74**	**-**

D.H.D-1	45.74	3.52	32.84	10.18	4.67	1.64	1.41	-
D.H.D-2	34.82	3.60	36.04	14.75	4.88	2.55	3.35	-
D.H.D-3	45.61	3.18	32.27	10.78	4.53	1.67	1.96	-
D.H.D	**42.06**	**3.43**	**33.72**	**11.90**	**4.69**	**1.95**	**2.24**	**-**
D.H.D (agg.)-1	1.30	2.01	65.84	15.91	8.31	3.08	3.56	-
D.H.D (agg)-2	1.35	2.08	69.66	14.12	6.67	2.81	3.30	-
D.H.D (agg)-3	2.03	1.78	73.54	12.24	5.70	2.07	2.63	-
D.H.D (agg.)	**1.56**	**1.96**	**69.68**	**14.09**	**6.89**	**2.65**	**3.16**	**-**
D.Br-1	3.07	2.67	57.55	18.77	12.73	2.34	-	-
D.Br-2	3.33	2.56	57.88	19.03	12.31	2.04	-	-
D.Br-3	4.43	2.52	57.74	19.60	11.63	1.52	-	-
D.Br	**3.61**	**2.58**	**57.72**	**19.13**	**12.22**	**1.97**	**-**	**-**