CHARACTERIZATION OF SELECTED BEYLIKLER PERIOD MORTARS AND PROCESSING OF NEW INTERVENTION MORTARS FOR RESTORATION PURPOSES

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ABSTRACT

In this study, Saruhanlı Emirates period mortars collected from Manisa Çukur Hamam (Bath) and Manisa Hacet Mescidi (Mosque) in Western Turkey were characterized, and the results of characterization tests were used for production of new compatible mortars, which would then be used for conservation of the buildings. For this purpose, physical, mineralogical and chemical compositions of the mortars were characterized by XRD, SEM-EDS, TGA and chemical analysis. The results indicated that the mortars were hydraulic and were produced by the use of pozzolanic aggregates. The use of hydraulic lime mortars can be related to the structural requirements of these buildings. The binder aggregate ratio of mortar samples were in the range of 1:2-1:4. Aggregate particle sizes that are grater than the 1180 µm composed the largest sizes of the total aggregates and aggregates were composed of quartz, albite and anorthite. Lime aggregate ratios (L/Ag) of the produced intervention mortars were in the range of 1:6-1:1. Standard sand was used as aggregate. The pozzolanic additive was commercial clay, which was heat treated between 25 and 1000°C. It was found that the addition of K-244 clay which was heat-treated above 600°C improved compressive strengths of the mortars.

ÖZET

Bu çalışmada 14. yüzyıl Saruhanoğulları Beyliği dönemi yapılarından olan Manisa Çukur Hamam ve Manisa Hacet Mescidi'nden toplanan harç örnekleri fiziksel, kimyasal ve mineralojik olarak karakterize edilmiştir. Elde edilen sonuçlar yapılardan toplanan malzemelerle uyumlu çalışabilecek ve bu yapıların korunmasında kullanılabilecek potansiyel müdahale harçlarının hazırlanmasında kullanılmıştır. Uygulanan testler sonucunda harç örneklerinin hidrolik karakterde olduğu, puzolanik aggregalardan üretildiği ve bağlayıcı aggrega oranlarının 1:2-1:4 aralığında değişim gösterdiği saptanmıştır. Harç örneklerinde kullanılan aggregalar genel olarak boyutları 1180 μm'den büyük aggregalardan oluşmaktadır ve kuvars, albit ve anortit mineralleri içermektedir. Karakterizasyon işlemi sonucu elde edilen bilgiler potansiyel müdahale harçlarının üretiminde kullanılmıştır. Hazırlanan harçların bağlayıcı aggrega oranları 1:6-1:1 aralığında değişmektedir ve aggrega olarak standard kum kullanılmıştır. Harç örneklerinin bir kısmı yapay puzolan kullanılarak, diğer kısmı ise doğal puzolan kullanılarak hazırlanmıştır. Yapay puzolan olarak 25-1000^{o}C aralığında ısıl işlem uygulanmış kil, doğal puzolan olarak ise ısıl işlem görmemiş kil kullanılmıştır. Kullanılan kil örneklerinden, K-244 kodlu 600^{o}C üzerinde ısıl işlem görmüş ticari kil örneğinin harcın basma dayanımını arttırdığı saptanmıştır.

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CHAPTER 1

INTRODUCTION

Conservation works should prevent decay and prolong the life of cultural and natural heritage. The minimum effective intervention is always the best; if possible, the action should be reversible and not prejudice possible future interventions. Any building conservation project depends to a large extent on studies of the original building materials and particularly on their methods of manufacture, the sources and extraction of their raw materials, and their deterioration. Conservation of architectural heritage requires multi-disciplinary approach. A full understanding of the structural and material characteristics is required in conservation practice. The characteristics of materials used in restoration work and their compatibility with existing materials should be fully established.

Incompatible cement based mortars were used frequently as restoration materials in Turkey. These materials were too strong, had larger thermal expansion, lower porosity and formed soluble salts while setting. Due to these unconscious interventions, ancient structures have been damaged and now many structures are in a damaged situation.

The subject of this study was two fold. First a determination of the characteristics of lime mortars collected from Manisa Çukur Hamam(Turkish Bath) and Manisa Hacet Mescidi (Mosque) was done. And information collected in the first phase was used for production of potential intervention mortars which can be used in restoration of these two structures.

Mortar samples collected from walls and domes of the two structures. Different types of analyses were applied to these materials. The aim of analyses were determination of physical properties, mechanical properties, raw material compositions, pozzolanic activity, mineralogical compositions, chemical compositions, microstructural properties and determination of hydraulicity of mortars. The results of these analyses have been used for the determination of properties of the possible intervention mortars for these two structures. After the determination of characteristics of intervention mortars, the mortars were produced and characterized for determination of the possibility of applicability.

This thesis is hence composed of five chapters. In Chapter II, a brief information is presented on lime mortars. In Chapter III the experimental procedure for characterization of materials collected from structures and the manufacturing procedure of intervention mortars are given. Chapter IV presents the results obtained from the experiments and the discussion of the results. The last chapter outlines the conclusions of the thesis.

CHAPTER 2

LIME MORTAR

Mortar is a term loosely applied to material used for bedding, jointing and rendering brickwork and stonework and it normally consists of lime or other binding material with or without suitable filler or fine aggregate (Davey 1961) .

The oldest mortar used for building was mud, and is still used in many countries throughout the world. In ancient Egypt mud mortar was used with sun-dried bricks, but for bedding the stonework of monumental buildings, gypsum was used (Davey 1961). Lime mortars were commonly used in buildings from Greek times through the beginning of the 19th century (Davey 1961).

It is commonly supposed that the purpose of a mortar is to stick masonry units together, but this is only a minor part of the work to be done. The joints between the units should provide a cushion to spread the loads evenly, particularly with soft bricks and stones. They should act like a wick to draw moisture out of a wall and provide a good surface for evaporation. In this way they will take harmful soluble salts away from the masonry units and can act as a sacrificial material; the wall can then be repaired by simple process of repointing the joints. For drawing moisture out of the wall, the mortar must be softer, more porous, and more permeable than the masonry units (Holmes and Wingate 1997, Lynch 1994). Soft mortar can contribute to long life by tolerating the small deformations in a building. All buildings move, both from temperature changes and from variations in the firmness of the ground below their foundations (Holmes and Wingate 1997, Allen et al. 2003). The soft lime mortars have self-healing properties. The free lime in the mortars crystallizes and carbonates to heal cracks with the action of moisture.

Lime mortars consist of a binding agent (lime), filler or aggregate and water. Sand is the most common aggregate used in lime mortars. Lime is produced by the calcinations of limestone and slaking off quicklime.

2.1 Limestone

Lime is the widespread constituent of the greatest percentage of the ancient mortars. Lime in its variety of forms, is derived mainly from chalk or limestone (Lynch 1994).

Limestone is a naturally occurring mineral that consists principally of calcium carbonate. Combination of dissolved calcium ions and carbon dioxide resulted in the sedimentary deposition of calcium carbonate, which was subsequently converted into limestone rock. (Oates 1998, Boynton 1966).

Limestone is a general term embracing carbonate rocks or fossils; it is composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities, such as silica and alumina (Boynton 1966, Gay et.al. 1932).

The limestone may be composed of four minerals, exclusive of impurities, Calcite ($CaCO_3$), Aragonite ($CaCO_3$), Dolomite ($CaMg(CO_3)_2$) and Magnesite ($MgCO_3$) (Boynton 1966, Gay et.al. 1932).

Limestone is found in many forms and is classified in terms of its origin, chemical composition, structure, and geological formation (Oates 1998, Boynton 1966). The following eleven descriptions include the great majority of significant limestone deposits

- Biosparites
- Micrites
- Biomicrites
- Reef
- Algal
- Oolitic
- Dolomite
- Chalks
- Marble
- Travertine
- Tufa

Many limestones are remarkably pure with less than 5% of non-carbonate impurities. There are two classifications of impurities:

1. *Homogeneous*: In which the impurities in the form of clay, silt and sand, contaminate the stone when it is first deposited and in which the impurities are well dispersed throughout the formation
2. *Heterogeneous*: In which the impurities only in crevices or between the strata or as siliceous pieces or nodules of sand, chert or flint loosely embedded in limestone. This is the source of silica and alumina, the major impurities. A minor source of silica is derived from feldspar, mica, talc, and serpentine.

Iron is the third major impurity and can be homogeneously disseminated after the limestone has started to form by chemical displacement of the calcium, making iron carbonates. Phosphorus and sulphur usually occur but generally in small quantities. The remaining impurities are so minute that they could be considered as trace elements in relatively pure stone. These might be manganese, copper, titanium, sodium and potassium, fluorine, arsenic and strontium (Davey 1961, Boynton 1966).

2.1.1 Limestone Calcination

The term "calcination of limestone" refers to the process of its thermal decomposition into quicklime (CaO) and carbon dioxide (CO_2) (Rxn 1). The reaction for the thermal decomposition of calcium carbonate ($CaCO_3$) is written as ;

$$CaCO_3 + \text{Heat} \longrightarrow CaO + CO_2 \uparrow \qquad \text{(Rxn 1)}$$

There are three essential factors in the kinetics of limestone's decomposition (Boynton 1966):

- The stone must be heated to the dissociation temperature of the carbonates.
- This minimum temperature must be maintained for certain duration
- The carbon dioxide gas that is evolved must be removed.

The dissociation temperature of calcite is 898 ^{o}C (1648^{o}F) for 1 atm. Pressure and the end product is calcium oxide, “quicklime” sometimes described as “unslaked lime”.

After the calcination of limestone the product (quicklime (CaO)) should be cooled in an atmosphere free from carbon dioxide, a precaution necessary in order to avoid recombination (Cowper 2000)

Calcination of limestone takes place in kilns. Kilns subdivide into two general types, The Intermittent and Continuous (Figures 2.1-Figure 2.2). The design and operation of kilns have been metamorphosed from days of the ancient Egyptians into a modern chemical-process industry. The first kilns were field or pot kilns (intermittent type) and they were usually crudely constructed of stone, often on the side of a hill. They were of low height and had steel plates at the top serving as wind break (Boynton 1966, Cowper 2000, Ashurt et.al 1990, PULM 1995). Stone was placed through the top of the kiln with the largest stone introduced first forming an arch. Layers of increasingly smaller stone where then added, a wood fire was ignited in the hearth below, later supplemented with coal or more wood. After burning three to five days, the fire was extinguished and the lime was drawn after cooling. The next major improvement was the vertical mixed-feed kiln (continuous type) of greater height and capacity. These were at first crudely constructed with fieldstone, but unlike the field kilns, since these kilns were largely continuous, they were usually lined with refractory brick. Alternate layers of stone and fuel (coal, coke, or wood) were charged into the top of the vertical stack. As a layer of stone was calcined, it was drawn at the bottom and additional stone and fuel were added at the top. Such kilns improved fuel efficiency and capacity and were inexpensive to construct. (Boynton 1966, Cowper 2000).

Since 1900 there have been almost countless varieties of patented kilns invented and promoted. Modern kilns can be classified as; vertical, rotary and miscellaneous (Oates 1998). In these kilns, oil and gas are used as fuel and calcinations of limestone takes places at high temperatures. Therefore, there is disadvantage of quicklime to become over-burnt (Ashurst et.al 1990).

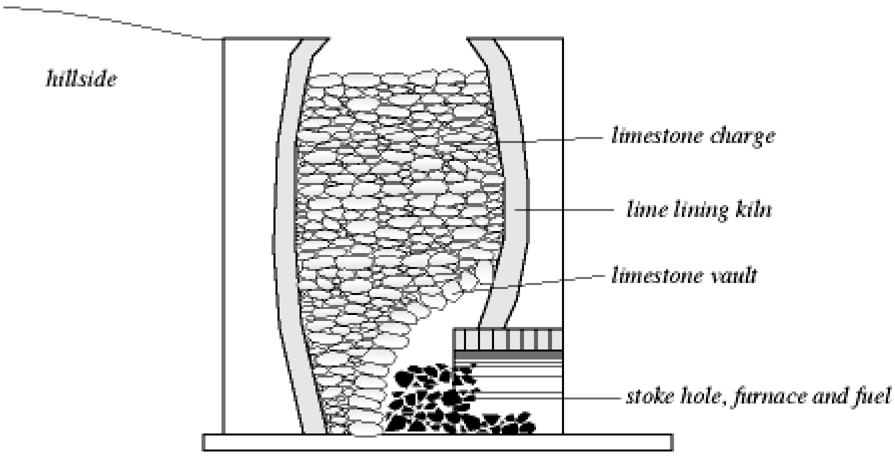


Figure 2.1. The intermittent type of limestone calcinations kiln
(Source: Davey 1961)

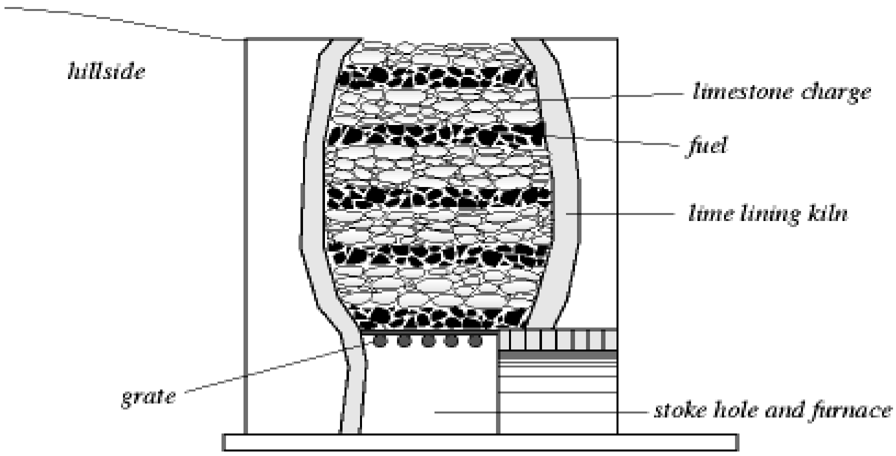


Figure 2.2. The continuous type of limestone calcinations kiln
(Source: Davey 1961)

2.1.2 Lime Hydration (Slaking)

Slaking is the reaction of the quicklime with water. During the process, hydroxide of calcium are formed by the action of water on oxides (Rxn 2).

$$CaO \text{ (High Calcium Quicklime)} + H_2O \longrightarrow Ca(OH)_2 \text{(High Calcium Hydrate)} + \text{Heat} \uparrow \qquad \text{(Rxn 2)}$$

In slaking process, as the water penetrates into the surface pores, heat of hydration is triggered. This exerts great internal expansive force in the lime particle and causes it to fracture, shatter, and then disintegrate completely into countless micro particles, either as crystalline dust (dry hydrate) or as colloidal suspension (lime putty), the difference depends on the amount of water added (Boynton 1966, Lynch 1994). Traditionally, this process was carried out in pits and slaked lime was left to mature for several months or even years (Ashurst et.al. 1990).

2.1.3 Factors Affecting the Quality of CaO and Slaking Efficiency

Calcination conditions have important effects on the quality of quicklime (CaO). Chemical compositions of limestone, temperature of kiln during calcination, residence time of kiln and the extent of CO_2 in the kiln atmosphere are the major determinants of the quality of CaO (Quicklime) (Hassibi 1999).

Slaking temperature, lime to water ratio, degree of agitation during slaking, viscosity of slurry, slaking time, and water temperature affect slaking efficiency of quicklime (CaO) by affecting the specific surface of the calcium hydroxide ($Ca(OH)_2$), directly or indirectly (Hassibi 1999).

2.2 Types of Lime

The type of lime available is dependent on the composition of the limestone from which it is produced and on the techniques of production. Historically the available range included non-hydraulic, through feebly, moderately and eminently hydraulic limes, magnesian limes and natural cements (Boynton 1966).

2.2.1 Non-hydraulic Limes

Non-hydraulic limes also known as air limes, are so called because they will not set chemically under water but require exposure to carbon dioxide in air in order to harden. Such limes are produced from limestone, which are relatively sources of calcium carbonate ($CaCO_3$), but which may contain varying amounts of magnesium carbonate ($MgCO_3$). (EHDBL 1997, PULM 1995).

Non-hydraulic limes are broadly classified by their chemical content and by their purity. In general, a distinction can be drawn between Calcium Limes, which contain

85% or more of calcium oxide and Magnesian Limes, which contain over 10 to 20% of magnesium oxide (EHDBL 1997). As regards purity, the common classification is as follows:

- Fat Limes: Contain 5% or less of impurities such as clay (silica and alumina). Such limes slake rapidly, producing much heat, and double or more increase in volume during the process.
- Lean Limes: Contain more than 5% of impurities and therefore less pure than fat limes. Lean limes slake more slowly than fat limes, with a smaller increase in volume.

Non-hydraulic limes rely for their hardening on drying and on the absorption of carbon dioxide. The resultant gradual conversion of calcium hydroxide to calcium carbonate requires an optimum balance of moisture and temperature, and may take many years to complete (EHDBL 1997, PULM 1995).

2.2.2 Hydraulic Limes

Hydraulic limes set by chemical reaction with water and so differ from non-hydraulic limes, which harden by reaction with carbon dioxide in the air. Thus, hydraulic limes are capable of setting and hardening under water. The raw material for hydraulic limes is limestone, but limestone, which naturally contains a proportion of clay in addition to calcium and magnesium carbonates (EHDBL 1997, PULM 1995).

Hydraulic limes have traditionally been classified by the amount of active clay materials they contain, as indicated below:

Classification	**Active Clay Materials**
Feebly hydraulic	<12%
Moderately Hydraulic	12%-18%
Eminently Hydraulic	18%-25%

In general, speed of set in water and ultimate compressive strength achieved will increase with higher levels of hydraulicity. Thus, a feebly hydraulic lime will set slowly and achieve a lower compressive strength than eminently hydraulic lime (EHDBL 1997, PULM 1995).

2.3 Aggregates

Aggregates used in traditional lime mortars include natural sands and gravels and crushed materials such as shell, various types of rock, brick, and old crushed lime mortar (PULM 1995, Lynch 1994). Aggregates generally comprise big part of volume of a lime mortar and the characteristics of the aggregate chosen are critical to the performance of the mortar.

Aggregates in lime mortar perform a number of functions;

- They act as filler, reducing the amount of lime needed, and thereby reducing drying shrinkage in the mortar.
- They may act as air entrainers and thus contribute some degree of frost resistance to the mortar.
- Their air entraining properties may influence carbonation and hardening of the mortar.
- They contribute to compressive strength.
- Aggregates containing pozzolanic materials introduce a degree of chemical set to he mortar

The nature of aggregate used in a mortar is critical to the workability and performance of the mortar. For the best performance and workability, aggregates should be well-graded sharp sand containing a balanced range of particle sizes and shapes, allowing all the grains to fit together and interlock into a well-bonded mortar (PULM 1995).

2.4 Pozzolanas

The term pozzolana is used to describe those siliceous or siliceous aluminous materials, which in themselves possess little or no cementitous value, but will gain cementitous property when they are in a finely divided form and react with calcium hydroxide in the presence of moisture (Davey 1961).

The reaction that takes place between finely divided pozzolana and calcium hydroxide, in the presence of moisture, can be shown as follows (Rxn 3);

$$\underset{\textit{Calcium Hydroxide}}{CH} + \underset{\textit{Silica}}{S} + \underset{\textit{Water}}{H} \longrightarrow \underset{\textit{Calcium Silicate Hydrate}}{C-S-H} \qquad \text{(Rxn 3)}$$

Calcium silicate hydrate (C-S-H) is the hydration product in very finely divided state and because of its extra ordinary high surface area; it provides binding property (Lea 1940).

2.4.1 Classification of Pozzolanic Materials

The name pozzolana was originally used for vitreous pyroclastic material produced by violent eruptive volcanic action. It is now used as a generic term to describe all materials which exhibit reactivity with lime and which set, harden, and develop strength in the presence of water (Davey 1961). Pozzolanas may be divided into two separate groups, the one consisting of natural pozzolanas and the other of artificial product (Lea 1940, Cowper 2000). Natural pozzolanas include such materials as some diatomaceous earths, opaline cherts and shales, tuffs and volcanic ashes or pumicites. The artificial pozzolanas are mainly products obtained by the heat treatment of natural materials such as clays and shales and certain siliceous rocks and pulverized fuel ash (fly-ash) (Lea 1940).

The natural pozzolanas are generally of volcanic origin, but include also certain diatomaceous earths. Volcanic origin pozzolanas are composed of a mixture of silicates and contain both glass and crystalline particles (Lea 1940). The diatomaceous earths, which form another class of natural pozzolanas, composed of the siliceous skeletons of diatoms deposited from either fresh-or-sea-water. The main constituent of diatomaceous earth is opal, which is an amorphous form of hydrous silica. (Lea 1940).

It is now generally agreed that the active part is the amorphous or vitreous portion and to a lesser extent the partially altered minerals, and that little activity can be attributed to the crystalline components which are stable inert compounds (aggregates) for lime (Lea 1940).

Many artificial materials possess some pozzolanic properties, but in most cases these properties are not sufficiently developed, or uniform, to make the materials of practical value. It has been known since Roman times that clays burnt at a suitable temperature have pozzolanic properties and such materials have long been in use in India and Egypt under the names of *Surkhi* and *Homra*. Materials such as clay burnt for ballast and ground clay bricks and tiles are to be regarded as aggregates possessing some useful pozzolanic properties, but as, in most cases, of little value for use as a true pozzolana (Lea 1940).

The chemical activity of pozzolana is dependent essentially on the presence of silica and alumina in such a condition, combined or free, that reaction with lime in solution proceeds with adequate speed. The rate of strength development of pozzolanas in lime mortars is influenced considerably by the fineness of grinding (Lea 1940). When the pozzolanas used in coarse state, the coarse particles act as more or less inert aggregate, which grades down to a fine dust, as an active pozzolana the activity of all pozzolanas is increased by fine grinding (Lea 1956).

2.4.2 Artificial Pozzolanas

The artifical pozzolanas were produced by the heat treatment of natural materials such as clay, certain siliceous rocks, and ground fly ash (Lea 1940). The most common artificial pozzolana is obtained by the heat treatment of clay. The clay is composed of oxides like silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3), which combine to form minerals like kaolinite ($Al_2O_3.2SiO_2.2H_2O$) and quartz(SiO_2). The crystal structure of clay minerals with a few exceptions, consist of sheets firmly arranged in structural layers (Konta 1995). The individual layers are composed of two, three, or four sheets (Konta 1995). The sheets are formed either by tetrahedrons $[SiO_4]^{4-}$, abbreviated as “T” or by octahedrons, e.g $[AlO_3(OH)_3]^{6-}$, abbreviated as “O”. The interior of tetrahedrons and octahedrons contain smaller metal cations, their apices being occupied by oxygens which are with protons (as OH). All these fundamental structural elements are arranged to form a hexagonal network in each sheet. According to the number and the ratio of sheets in a fundamental structural layer, the existing cation substitutions in the octahedrons and tetrahedrons and the resulting charge of the layers, the crystalline clay minerals are classified (Konta 1995).

2.4.3 Heating of Clay

The sequence of chemical reactions during the firing of clay, ignoring the removal of nonchemically bound species; such as water and organics can be outlined for kaolinite, which is widely present in the earth, as follows (Sujeong et.al. 1999, Palacio et.al.1996, Carty et.al. 1998, Iqbal et.al. 1999);

1. The crystal structure of kaolinite contains hydroxyl groups and the dehydroxylation of these groups to form metakaolin ($Al_2O_3.SiO_2$) occurs at around 550°C (Rxn 4).

$$Al_2O_3.2SiO_2.2H_2O \xrightarrow{550^o C} Al_2O_3.2SiO_2 + 2H_2O \uparrow \qquad \text{(Rxn 4)}$$

Dehydroxylation kinetics, believed to be first order, yields a dehydroxylation rate directly proportional to the surface area of kaolin. The dehydroxylation process is an endothermic process that is accompanied by reorganization of octahedrally coordinated aluminum in kaolinite to a mostly tetrahedrally coordinated aluminum metakaolin.

2. The α to β-quartz inversion occurs at 573°C.
3. Metakaolin transforms to a spinel-type structure and amorphous silica at ~950-1000°C (Rxn 5, Rxn 6).

$$3(Al_2O_3.SiO_2) \xrightarrow{\sim 950-1000^o C} \underset{A}{0.282 Al_8 (Al_{13.33} \oplus_{2.66}) O_{32}} + 6SiO_2 \qquad \text{(Rxn 5)}$$

$$3(Al_2O_3.2SiO_2) \xrightarrow{\sim 950-1000^o C} \underset{B}{0.562 Si_8 (Al_{10.67} \oplus 5.33) O_{32}} + 3SiO_2 \qquad \text{(Rxn 6)}$$

⊕: Vacancy

A: γ-Alumina type phase

B: Aluminosilicate spinel

4. Between 925-1000°C decomposition of clay relicts forms fine primary mullite (Rxn 7, Rxn 8). This reaction is strong exothermic reaction.

Aggregate of mullite crystals coming from the clay relicts are referred to as primary mullite, whereas the long needle shaped mullite crystals are termed as secondary mullite. For primary mullite Al_2O_3:SiO_2 ratio 2:1 for secondary mullite it is 3:2. The chemical reactions describing the conversion to mullite are;

$$0.282 Al_8 (Al_{13.33} \oplus_{2.66}) O_{32} + \xrightarrow{\sim 925-1100^o C} 3(Al_2O_3.2SiO_2) + 4SiO_2 \qquad \text{(Rxn 7)}$$

$$0.562 Si_8 (Al_{10.67} \oplus_{5.33}) O_{32} \xrightarrow{\sim 925-1100^o C} 3(Al_2O_3.2SiO_2) + 4SiO_2 \qquad \text{(Rxn 8)}$$

5. At ~1200 ^{o}C, the melt becomes saturated with silica-quartz dissolution ends, and quartz to cristobalite transformation begins.
6. Above 1200 ^{o}C mullite crystals grow as prismatic crystals.

The metakaolinite which forms at around 550 ^{o}C has important role in production of hydraulic mortar. Mixing of reactive metakaolinite (as artificial pozzolana) with lime and water results in the formation of a series of hydrated calcium aluminates and calcium silicates, which are responsible for the hydraulic properties of the mortar (Moropoulou et.al 2004).

2.5 Additives

Additives are mixed into mortars either to impart particular physical properties to the fresh or hardened mortars, or to give a colored finish to mortar. The additives include casein from milk, the whites of eggs, boiled linseed oil, fresh blood, keratin from horses' hooves, tallow from animal fat, beeswax, malt, beer and urine. These additives predicted to have been used for extension and retention of setting time, improvement of strength of mortar and improve the workability of mortar (Lynch 1994, Cowper 2000).

2.6 Lime Mortar Making

The basic ingredients of traditional lime mortars are lime and aggregate (sand), compressed and beaten together and matured before use. The quality and hence the potential performance of traditional lime mortars are improved by maturing before use (PULM 1995). Traditionally varieties of different methods have been adopted for combining sand and lime into mortars (PULM 1995, Ashurt et.al. 1988).

The mixing proportion of lime and aggregate depends on the grading of aggregates and plasticity of lime putty. The general mixing proportion have been used in traditional mortars was one part of lime putty to three parts of aggregate (Holmes et.al. 1997). This mixing proportion is for the good materials and for sharp sands. If the aggregate is rounded or is not well graded, or if the plasticity of lime is not good, proportion of lime can be increased. However, increment of lime proportion should be under control, because the excess lime can cause shrinkage cracks (Holmes et.al. 1997).

2.7 Hardening of Non-hydraulic Lime Mortars

The hardening of non-hydraulic lime mortars was known as “carbonation”. The carbonation is the reaction of calcium hydroxide with carbon dioxide in the air forming calcium carbonate (Figure 2.3) (Ashurt et.al 1988, Holmes et.al.1997). Carbonation is a delicate process, which is dependent on many factors including temperature, moisture, the thickness, and pore structure of the mortar and presence of carbon dioxide. Carbonation will begin while the mortar is still drying out and continue for many years (Ashurt et.al.1998, Holmes et.al.1997).

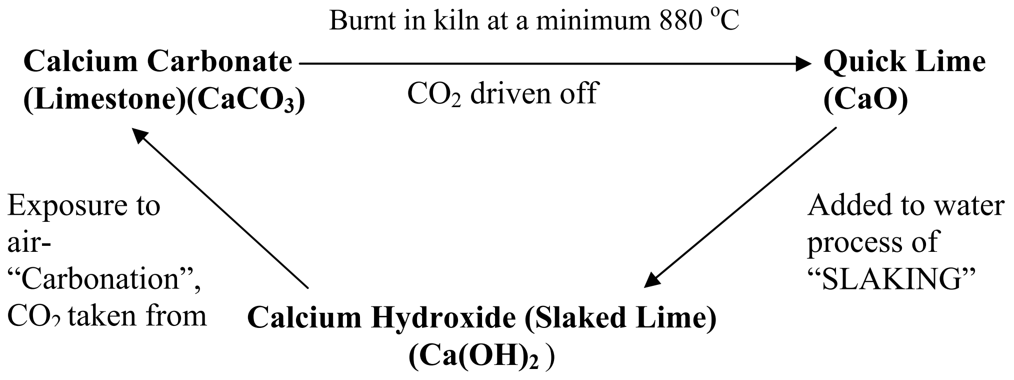


Figure 2.3. Burning, slaking and hardening of non-hydraulic lime

2.8 Hardening of Hydraulic Lime Mortars

Hydraulic mortars harden by chemical reaction with water. Pozzolanic materials produce a hydraulic reaction with slaked lime ($Ca(OH)_2$) due to their reactive silica (SiO_2) and alumina (Al_2O_3). Calcium silicate hydrate, a product of this reaction, forms an interlocking network of fibrous crystals or gel, which is the main cause of hardening of the mortar (Ashurt et.al. 1988, Davey 1961). Because of the presence of copious amounts of water on the left side of Rxn.3, these hydraulic lime mortars are perfectly suited for applications in humid areas like baths and waterfront properties. Such humid environments assure that the reaction 3 proceeds to the right, producing C-S-H products.

CHAPTER 3

EXPERIMENTAL METHODS

Mortar, brick and plaster samples, collected from Manisa Çukur Hamam (Bath) and Manisa Hacet Mescidi (Mosque) were characterized for determination of the properties, and the results of characterization tests were used for the estimation of properties of intervention mortars.

3.1 Çukur Hamam (Turkish Bath)

Çukur Hamam was built by İshak Çelebi in the fourth quarter of XIV. Century in Manisa (Turkey) (Figure 3.1) (Acun 1985, MKTV 1992). Superstructure consists of three big and five small domes in a square plan. There are three parts in Çukur Hamam; dressing hall, tepidarium and calidarium. Walls of the bath are built in brick, rubble stone, and mortar. Domes and arches of the bath are constructed with brick and mortar. There is no decoration inside and outside of the bath.

Figure 3.1. View from the west side of Çukur Hamam (Turkish Bath)

3.2 Hacet Mescidi (Mosque)

Hacet Mescidi was constructed in XIV. Century in Manisa (Turkey) (Figure 3.2) (Acun 1985, MKTV 1992). The mosque is in square plan and has a dome. Wall of the mosque are composed of rubble stone and mortar while dome is made of brick and mortar. Today the mosque is in tumbledown situation and filled with rubble up to the dome level.

Figure 3.2. South view of Hacet Mescidi (Mosque)

3.3 Characterization of Samples Collected from Manisa Çukur Hamam and Hacet Mescidi

The laboratory analyses of the mortars and bricks included the determination of physical properties, mechanical properties, raw material compositions, pozzolanic activity, mineralogical compositions, chemical compositions, microstructural properties and determination of hydraulicity of mortars. Physical property analysis covered the density and porosity tests, mechanical property analysis included uniaxial compressive strength and modulus of elasticity tests. Raw material composition and mineralogical properties of the mortars were determined by thermogravimetric analysis (TGA), chemical analysis and particle size distribution (PSD).

Chemical analysis involved the determination of binder aggregate proportions and pozzolanic activity measurement of fine aggregates.

3.3.1 Sampling

Mortar samples were taken, using hammer and chisel, from upper parts of Çukur Hamam and Hacet Mescidi to avoid such phenomena caused by capillary rise. The analyses were carried out in a significant quantity of samples in order to avoid errors caused by heterogeneity. The sample identification codes and the function of the mortar in structures are summarized in Table 3.1.

Table 3.1. Sample codes and identification

Sample Codes	**Identification**
Ç-M-BB1	Brick Masonry Mortar (Dome starting point)
Ç-M-BB2	Brick Masonry Mortar (Dome)
Ç-B	Brick (Dome)
Ç-M-SS	Stone Masonry Mortar (Entrance Gate)
Ç-P	Original layer plaster from Halvet
Ç-P2	Second layer plaster on original layer from same Halvet
Ç-L-P	3rd layer lime plaster from same Halvet
Ç-M-BB3	Brick Masonry Mortar (Dome)
H-B	Brick (Dome)
H-M-BB	Brick Masonry Mortar (Dome)
H-M-SS	Stone Masonry Mortar (Outer Wall)
Ç: Çukur Hamam, **H**: Hacet Mescidi, **M**: Mortar, **S**: Stone, **B**: Brick, **P**: Plaster**, L**: Lime	

3.3.2 Determination of Physical Properties

Physical properties of the samples were determined by density and porosity tests which are based on the RILEM Standard Test Methods (RILEM 1980). For determination of physical properties 3 pieces from each sample were dried in an oven at 60°C for 24 hours and weight of the samples measured after drying by a precision balance (AND HF-3000G) for determination of dry weights (M_{dry}). Then the samples were saturated with distilled water in a vacuum oven (Lab-Line 3608-6CE) and saturated weights of samples were measured (M_{sat}). Afterwards saturated samples' weights measured in distilled water (M_{arch}). The results were used for calculation of porosities (P%) and bulk densities (D) of samples by following formulas:

$$\mathrm{P}(\%) = \left[\frac{(M_{sat} - M_{dry})}{(M_{sat} - M_{arch})} \right] * 100$$

$$\mathrm{D}(\mathrm{g/cm}^3) = \left[\frac{M_{dry}}{(M_{sat} - M_{arch})} \right]$$

3.3.3 Determination of Mechanical Properties

Determination of mechanical properties were done by uniaxial compressive strength and modulus of elasticity tests (ISRM 1981, Ulusay et. al. 2001). Uniaxial compressive strengths of mortars, bricks and intervention mortars were measured by Shimadzu AG-I Mechanical Test Instrument. Uniaxial compressive strength tests were applied to three cubic specimens from each sample, which were free from crack (Figure 3.3). Specimens were prepared by using a cutting machine (Discoplan-TS 372). Care was taken to have parallel upper and lower surfaces. A 3mm rubber pad was placed on top and bottom of the samples to avoid stress concentrations on the specimen surface and to uniformly distribute the stress on the specimen's surface. Shimadzu AG-I Mechanical Test Instrument automatically computed, displayed and recorded test results using software system. Maximum force magnitude was configured as 15 kN and test speed as 3 mm/min. The instrument recorded strokes under continuous compression loading and the result of test used for calculation of uniaxial compressive strength by the formula;

$$\sigma = \frac{F}{A}$$

σ: Compressive strength ($\mathrm{kN/mm}^2$)

F: Failure Load (kN)

A: Area onto which loading was applied (mm^2)

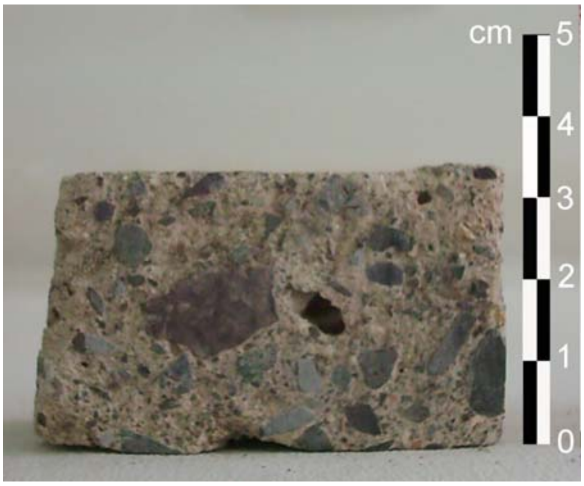


Figure 3.3. Mortar sample Ç-M-BB2 for the compressive strength test

Modulus of elasticity (Young’s Modulus) is the materials resistance to elastic deformation. The modulus of elasticity (E) is calculated as;

$$E = \frac{Stress}{Strain} = \frac{\sigma}{\varepsilon} = \left(\frac{\Delta F}{A}\right) \Big/ \left(\frac{\Delta l}{l_o}\right)$$

where;

ΔF : Failure load (kN)

A : Area which force was applied (mm^2)

Δl : Change in thickness of the sample along its vertical axis (mm)

l_o : Initial thickness of the sample (mm)

3.3.4 Determination of Percent Soluble Salt Content

The soluble salt content was determined by electrical conductivity measurements (Black 1965). For this purpose 1 g of dried and powdered sample was dissolved in 50 ml of distilled water. Total soluble salt content was determined by electrical conductivity measurements of salt extract solution by using conductometer (WTW MultiLine P3pH/LF). Percentage of soluble salts in samples were calculated by the following formula (Black 1965):

$$\text{Soluble Salt (\%)} = \left(\frac{A * V_{sol}}{1000}\right) * \left(\frac{100}{M_{sample}}\right)$$

$$\text{A= Salt Concentration} \left({}^{mg}\!/_{ml}\right) = 640 * \text{EC}$$

EC = Electrical Conductivity $\left({}^{mS}\!/_{cm} = {}^{mmho}\!/_{cm} \right)$

V_{sol} = Volume of the solution (ml)

M_{sample} = Weight of the sample (mg)

3.3.5 Determination of Raw Material Properties

Raw material property of mortar samples was determined by binder/aggregate ratio and particle size distribution analyses.

3.3.5.1 Binder Aggregate Ratios of Mortars

The binder aggregate ratios of mortar samples were determined by treatment of samples by dilute hydrochloric (HCl) acid (Jedrzejevska 1981, Middendorf and Knöfel 1990). Three pieces of 50-60g from each mortar sample were dried and weighed (M_{sample}) by precision balance and dissolved in (5%) HCl solution. Insoluble part was filtered and washed by distilled water, dried and weighed (M_{agg}). Acid soluble and insoluble parts were calculated by the following formula;

$$\text{Soluble Part (\%)} = \left[\frac{\left(M_{sample} - M_{agg} \right)}{M_{sample}} \right] * 100$$

Insoluble Part (%) = 100-[Soluble Part (%)]

M_{sample} : Weight of mortar sample

M_{agg} : Weight of aggregates

The calculated acid soluble part ratio by the formula above is not the exact ratio of lime, it also includes the ratio of calcareous aggregates that could be used in the mortar so the real aggregate and lime ratio were calculated by the formula;

$$\text{Aggregate }\% = \frac{100 * \text{Insoluble Part } (\%)}{\dfrac{(\text{Acid Soluble Part } \% * MW_{Ca(OH)2})}{MW_{CaCO3}} + \text{Insoluble Part } \%}$$

Lime %= 100- Aggregate %

$MW_{(CaCO3\,)}$: Molecular Weight of $Ca(CO)_3$

$MW_{Ca(OH)2\,:}$ Molecular Weight of $Ca(OH)_2$

3.3.5.2 Particle Size Distribution of Aggregates

Determination of particle size distribution of aggregates was carried out by standard sieving test with 1180 µm, 500 µm, 250 µm, 125 µm and 53 µm sizes of sieves (Teutonico 1988). Aggregate samples were placed on the above mentioned stack of sieves which were shaken for 30 minutes by using an analytical sieve shaker (Retsch AS200). Weight of the aggregates retained on each sieve was weighed and the percentages were calculated.

3.3.6 Pozzolanic Activities of Aggregates

Determination of pozzolanic activity of fine aggregates (<53µm) was obtained by measurement of electrical conductivity of samples. For this purpose first of all the electrical conductivity of saturated calcium hydroxide solution ($Ca(OH)_2$) was measured. Then sample was added to saturated calcium hydroxide solution ($Ca(OH)_2$) at room temperature with the sample solution ratio of 1g/40ml and stirred. The fastest reaction occurred in first 2 minutes. Afterwards the mixture conductivity was measured. Reaction took place between sample and calcium hydroxide solution was caused to difference in electrical conductivity. The difference in measured electrical conductivity was used to express the pozzolanic activity. The samples that showed electrical conductivity differences in excess of 1.2 mS/cm presented good pozzolanicity (Luxan et al. 1989).

3.3.7 Chemical, Mineralogical and Microstructural Properties of Samples

Mineralogical compositions of samples collected from two structures and the intervention mortars produced were determined by X-ray Diffraction (XRD) analysis by using Philips X-Pert Pro X-Ray Diffractometer (CuKα radiation) in the range of 2-70^o 2θ. Mortar samples collected from the two structures were first visually characterized by a trinocular stereo zoom microscope (Olympus SZ40) equipped with video camera.

Chemical compositions and microstructural properties of binder, aggregate, possible reaction products that formed in-between, white lumps (unreacted lime), lime, clay and sand were determined by Philips XL 30S-FEG Scanning Electron Microscope (SEM) equipped with X-Ray Energy Dispersive System (EDS).

3.3.8 TGA Analysis of Samples

Thermogravimetric analysis (TGA) was performed at a temperature range of 30-1000^{o}C with a heating rate of 10^{o}C/min in nitrogen atmosphere. Analysis was performed by Shimadzu TGA-21 thermogravimetric analyzer. Thermogravimetric analysis was performed for determination of samples' hydraulicity, which depends on the weight losses in determined temperatures, and the structure of clay samples.

3.4 Manufacturing of Intervention Mortars

In this study, new mortars were produced in order to propose new compositions for potential intervention mortars that can replace deteriorated mortars in the structures. These new mortars were compatible with the originals as far as their composition and mineralogy. In historic structures, the matching of constituents of the mortar to those of original structure is very important. Therefore, the properties of intervention mortar constituents have to be well known.

3.4.1 The Lime Used in the Intervention Mortar

The lime used in preparation of mortar was supplied by Öztüre Kimtaş A.Ş Izmir, and was commercial hydrated lime powder.

3.4.2 The Aggregates Used in the Intervention Mortar

Çimentaş A.Ş has supplied the sand, which was used as aggregate in production of the mortar. That was commercial sand with known chemical and mineralogical composition per TS EN 196-1 standard.

3.4.3 The Pozzolanas Used in the Intervention Mortar

In preparation of intervention mortar heated clay material was decided to be used as pozzolana source. The commercial clay samples collected from Kalemaden A.Ş, Yüksel Seramik A.Ş, and Tamsa Seramik A.Ş in the form of granule or powder form. The samples were ground to sizes smaller than 100 mesh. The commercial codes of the clay samples are given in Table 3.2.

Table 3.2. The commercial codes of clay samples

Codes	**K-31**	**K-103**	**K-244**	**K-261**
Source	Tamsa Seramik A.Ş	Yüksel Seramik A.Ş	Kalemaden A.Ş	Kalemaden A.Ş

Commercial clay samples heated at varying temperatures of 400, 450, 500, 550, 600, 800, 1200 ^{o}C with a heating rate of 10^{o}C/min were used as pozzolanas.

3.4.4 Mortar Preparation

Mortar mixtures were prepared by the Kitchenaid® mini mixer (mono phase 5lt) (Figure 3.4).

Figure 3.4. Kitchenaid mini mixer ®

The binder aggregate (B/Ag) ratios selected for this study varied around the 1:3 as the most cited ratio in the literature. The B/Ag ratios used in preparation of mortar were 1:1, 1:3, 1:6 by weight. Table 3.3 presents the composition of lime mortar mixtures prepared in this study by following the procedure outlined in ASTM standard (ASTM C 109).

Table 3.3. The mixing ratio and the amount of pozzolanas used in preparation of mortar

Mortar Mix No.	**B/Ag Ratio**	**Amount of Lime (g)**	**Amount of Sand (g)**	**Amount of Pozzolana (g)**			
				K-103 (NP)*	**K-244 (25^oC)**	**K-244 (600^oC)**	**K-244 (1000^oC)**
1	1/6	180	1080	90	-	-	-
2	1/6	180	1080	-	-	90	-
3	1/3	180	540	90	-	-	-
4	1/3	180	540	-	90	-	-
5	1/3	180	540	-	-	90	-
6	1/3	180	540	-	-	-	90
7	1/1	180	180	90	-	-	-
8	1/1	180	180	-	-	90	-

*NP: Natural pozzolana

The temperature and humidity has important effect on mortar preparation procedure which was as follows (ASTM C 109);

a. The room temperature should be maintained between 20°C and 27.5°C and the temperature of the dry materials, paddle, and bowl shall be within the above range at the time of the test. Temperature of the mixing water shall not vary from 23°C by more than 1.7°C.

b. The relative humidity of the laboratory shall not be less than 50 percent.

Mortar mixtures should be prepared using correct amount of water required to obtain normal consistency and a good workability.

The mixing procedure for preparation of mortar was as follows (ASTM C 109);

a. Place all mixing water in the bowl.

b. Add the blended lime and pozzolana to the water and allow it to stand for 1 minute. Then start the mixer and mix at slow speed (140±5 rpm) for 30 seconds.

c. Add the entire quantity of sand slowly over a 30-second period while mixing at slow speed.

d. Stop the mixer change to medium speed (285±10rpm) and mix for 30 second.

e. Stop the mixer and let the mortar stand for 1.5 minute. During the first 15 second of this interval, quickly scrape into batch any mortar that may have remained on the sides; then for the remainder of this interval cover the bowl with lid.

f. Finish by mixing for 1 more minute at medium speed (285±10rpm).

g. In any case requiring a remixing interval, any mortar adhering to the side of the bowl should be quickly scraped down into batch with the scraper prior to remixing.

After the mixing procedure the samples were cast in cylindrical molds made from commercially available PVC pipes (R=5 cm, h=5 cm). Molding of mortar was applied according to the standard ASTM C 104. The applied molding procedure was as follows;

a. Start molding the specimens within a total elapsed time of not more than 2 minutes and 30 seconds after completion of the original mixing of the mortar batch.

b. Place a layer of mortar about 1 inch (approximately one half of the depth of mold) in all of the cube compartments.

c. Tamp the mortar in each cube compartments 32 times in about 10 second in 4 rounds, each round to be at right angles to the other and consisting of eight adjoining strokes over the surface of the specimen.

d. The tamping pressure shall be sufficient to ensure uniform filling of the molds.

e. The 4 rounds of tamping (32 strokes) of the mortar shall be completed in cube before going to next.

f. When the tamping of the first layer in all of the cube compartments is completed, fill the compartments with the remaining mortar and then tamp as specified for the first layer.

g. During tamping of the second layer bring in the mortar forced out onto the tops of the molds after each round of tamping by gloved fingers and tamper upon completion of each round and before starting the next round of tamping.

h. On completion of the tamping, the tops of all cubes should extend slightly above the tops of the molds. Bring in mortar that has been forced out onto the tops of the molds with trowel and smooth off the cubes by drawing the flat side of the trowel (with leading edge slightly raised) once across the top of each cube at right angles to the length of the mold. Then for the purpose of leveling the mortar and mixing the mortar that protrudes above the top of the mold of more uniform thickness, draw the flat side of the trowel (with leading edge slightly raised) lightly once along the length of the mold.

i. Cut off the mortar to a plane surface flush with the top of mold by drawing straight edge of trowel (held nearly perpendicular to mold) with a sawing motion over the length of the mold.

Storage of specimens applied according to standard ASTM C 593;

a. When molding is completed, place the filled mold in the glass container as shown in Figure 3.5. The samples were sitting in a steel rack immediately above a water pool at the bottom of the container which was maintained at 54±2 ^{o}C in a closed oven (Figure 3.5). The top surface of the container was covered with glass sheet to avoid loss of water during heating.

b. Allow the specimens in the molds to remain in the humid container for 7 days.

c. Remove the samples from the container and allow them to cool to 23±2 °C in air saturated sufficiently that no dry drying takes place during cooling.

d. When the specimens are cool, remove them from the molds, and store them at 23±2°C at 95 to 100 percent relative humidity until the time of the compressive strength test .

3.4.5 Storage of Intervention Mortars

Curing of mortar samples was done in a (44x44.5x35cm) glass cube (Figure 3.5) at 54±2 °C in 7 days in an oven (Nüve FN500) while the top of the glass container was sealed and covered by glass plate. Care was taken to maintain the same amount of water at the bottom of the container to produce a 100% humidity atmosphere. After 7 days the glass container was removed from the oven and kept on a laboratory bench at around 23±2 °C until the time of the compressive strength test.

Figure 3.5. Storage system of mortar samples

CHAPTER 4

RESULTS AND DISCUSSION

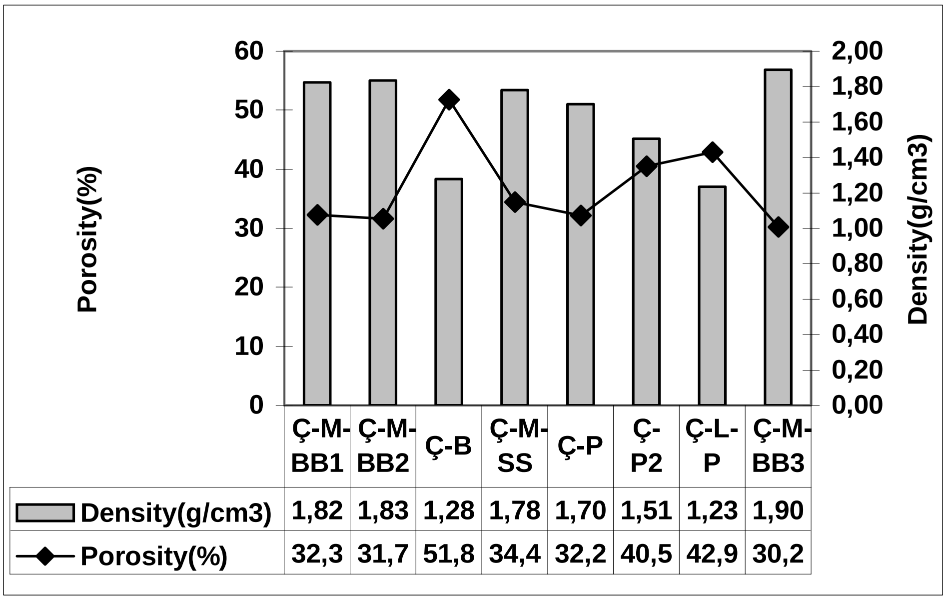
This chapter is composed of experimental study results of samples collected from Manisa Çukur Hamam and Manisa Hacet Mescidi, as well as results of the manufactured intervention mortars.

4.1 Properties of the Mortar Brick and Plaster Samples of Çukur Hamam and Hacet Mescidi

This part composed of the experimental study results of samples collected from Çukur Hamam and Hacet Mescidi. Density, porosity, soluble salt content of samples, lime aggregate ratios of mortar samples, particle size distribution of aggregates, pozzolanic activities of fine aggregates, mineralogical, chemical and microstructural properties of white lump samples, aggregates and mortars, hydraulic and mechanical properties of mortar samples are described and discussed in this chapter.

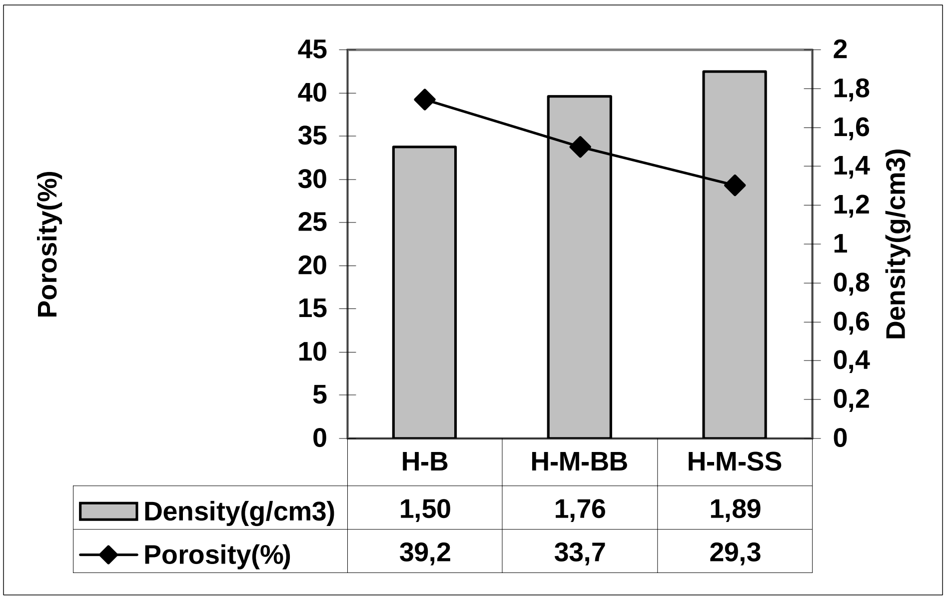
4.1.1 Density-Porosity Values of Mortar, Brick and Plaster Samples

Density values of stone masonry mortar samples collected from Çukur Hamam and Hacet Mescidi were 1.78 and 1.89 g/cm^3, and porosity values were 34.4 and 29.3 % by volume, respectively. Density of brick masonry mortars ranged between 1.76-1.90 g/cm^3 and porosity values were in the range of 30.2-33.7 % by volume (Figure 4.1 and Figure 4.2). Density values of plaster samples ranged between 1.23 and 1.70 g/cm^3 and porosity values were between 32.2%-42.9% by volume. Density values of bricks were 1.28 g/cm^3 for Cukur Hamam and 1.50 g/cm^3 for Hacet Mescidi samples and porosity values were 51.8 and 39.2 % by volume, respectively.



	Ç-M-BB1	Ç-M-BB2	Ç-B	Ç-M-SS	Ç-P	Ç-P2	Ç-L-P	Ç-M-BB3
▭ Density(g/cm3)	1,82	1,83	1,28	1,78	1,70	1,51	1,23	1,90
—◆— Porosity(%)	32,3	31,7	51,8	34,4	32,2	40,5	42,9	30,2

Figure 4.1. Density and porosity values of samples collected from Çukur Hamam



	H-B	H-M-BB	H-M-SS
▭ Density(g/cm3)	1,50	1,76	1,89
—◆— Porosity(%)	39,2	33,7	29,3

Figure 4.2. Density and porosity values of samples collected from Hacet Mescidi

When the density and porosity values of mortar samples from Çukur Hamam and Hacet Mescidi were compared with the brick samples, it was found that mortar samples presented higher density and lower porosity values than the brick samples. The purpose for the use of more porous and less dense bricks in dome structure are probably to obtain a lighter structure which is more resistant to earthquake (Moropoulou et al. 2002).

Density and porosity values of the mortar samples in this study were in the similar range with some other historic lime mortars from different periods of time (Moropoulou et al. 2004, Moropoulou et al.2003, Tunçoku 2001).

4.1.2 Soluble Salt Content of Mortar, Brick and Plaster Samples

It is widely accepted that salts contribute to the deterioration of building materials. Salt crystallisation is essentially a physical process, whereby salt solution is carried into the masonry from ground water or from pollutants. When salts, both soluble and insoluble, crystallize within the pores of fired clay bricks and mortars, stresses may develop that may be sufficiently large to cause cracking and local fragmentation of the materials. (Larbi 2004, Bucea et. al. 2003).

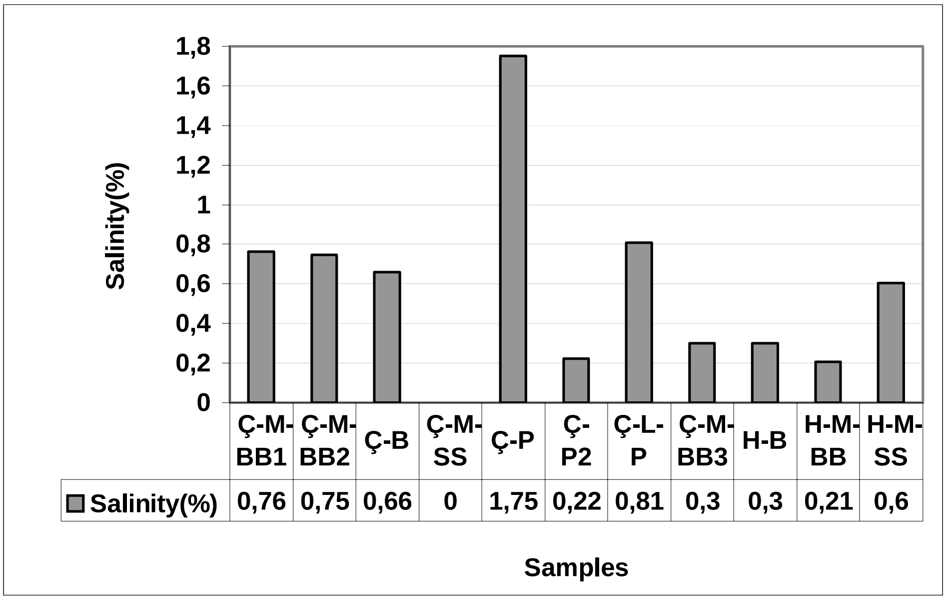


Figure 4.3. Soluble salt content (%) of samples collected from Çukur Hamam and Hacet Mescidi

Soluble salt concentration of the mortar and brick samples, which were collected from structures, were in the range of 0.21- 0.76% (Figure 4.3). Soluble salt content is one of the important signs of deterioration problems. As can be seen from the graph, all results were smaller than 1%, so it can be said that all the brick and mortar samples, that were collected from the two structures, were not deteriorated. However, one exception to this was for the plaster sample that was collected from Çukur Hamam (Ç-P), its soluble salt content was higher than 1% meaning that, it has deterioration problems.

4.1.3 Lime Aggregate Ratio of Mortar Samples

Ratio of lime and aggregates used in mortars is an important parameter influencing physical, mechanical and durability characteristics of mortar. The lime and aggregates should be in the right amount so that the mortar with good workability, durability and strength is produced (Davey 1961).

Table 4.1. Lime aggregate ratio of samples collected from Çukur Hamam and Hacet Mescidi

Samples	**% Lime**	**%Aggregate**	**Lime/Aggregate Ratio**
Ç-M-BB1	20	80	1:4
Ç-M-BB2	26	74	1:3
Ç-B	-	-	-
Ç-M-SS	32	68	1:2
Ç-P	63	37	1:1
Ç-P2	42	58	1:1
Ç-L-P	-	-	-
Ç-M-BB3	26	74	1:3
H-B	-	-	-
H-M-BB	35	65	1:2
H-M-SS	38	62	1:2

Lime ratio of the stone masonry mortars and brick masonry mortars that were collected from the Çukur Hamam and Hacet Mescidi were in the range of 20-38 % and the lime ratio of plasters collected from Çukur Hamam were 42% and 63% (Table 4.1). Stone masonry mortars of the structures presented high ratios of lime when compared with the brick masonry mortars. Lime aggregate ratio of the samples collected from Çukur Hamam and Hacet Mescidi were ranging between 1:2 to 1:4 per weight of mortar and 1:1 for plaster samples. These values were in the similar ranges of mortars and plasters used in some historic structures. (Moropoulou et al. 2005, Bakolas et. al.1998)

4.1.4 Particle Size Distribution of Aggregates Used in Mortar Samples

The natural sand is used as aggregates in mortars for masonry. Sand is a very important component of mortars, influencing considerably the performance of the formulations in which they are used. It is known that sand can have effects on many parameters such as workability, adhesion, mechanical properties and experience has shown that different types of sand lead to mortars with distinctive performances. The maximum particle size of the sand depends on the use of the mortar. The grain-size distribution of the sand should be continuous. The principle for grain-size distribution is that all the spaces between the larger particles are filled by smaller particles (Davey 1961, Henriques 2004, Sandin 1995).

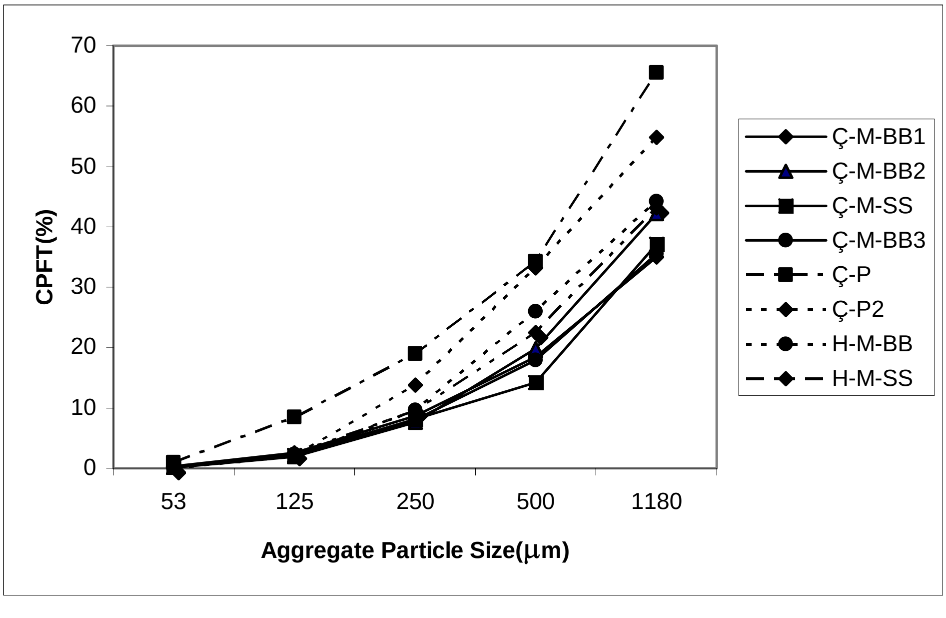
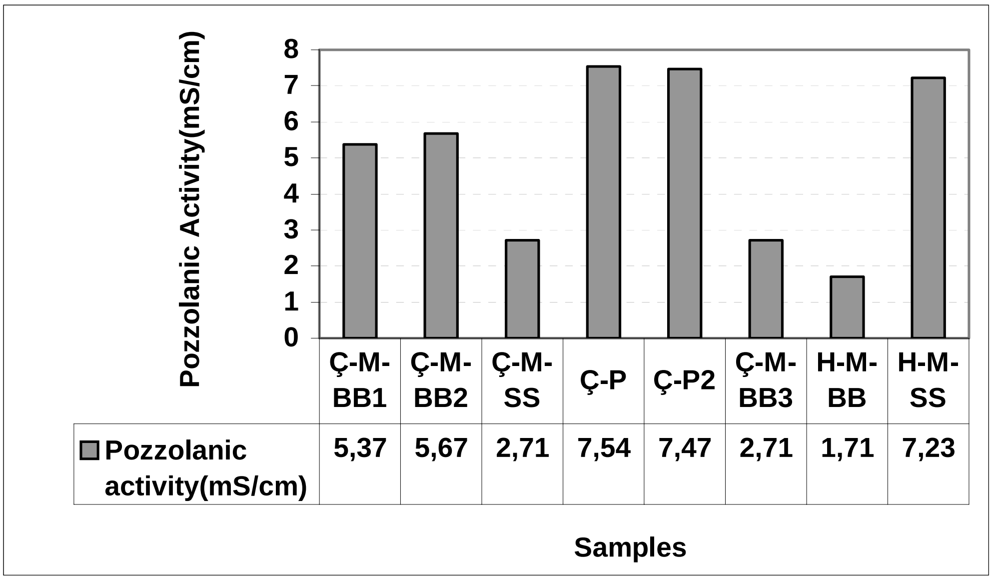


Figure 4.4 Particle size distribution of the aggregates used in mortars and plasters of Çukur Hamam and Hacet Mescidi
(CPFT: Cumulative percent finer than)

Grain size distribution of the aggregates of mortars after separation and sieving is shown in Figure 4.4. Aggregate particle sizes that are grater than the 1180 μm composed the largest portion of the total aggregates. This fraction ranged between 56%- 65% for brick masonry mortars and around 56% for stone masonry mortars, 40% for plasters. Fine aggregates (less than 125 μm) composed the fraction ranging between 2.1-2.4% for brick masonry mortars, around 2.3% for stone masonry mortars, and 5.3% for plaster samples. Plaster samples of Çukur Hamam were composed of fine aggregates (<1180□m) in high amounts..

4.1.5 Pozzolanic Activities of Fine Aggregates

Pozzolanic activities of the aggregates (<53μm) were obtained in the range of 1.71 mS/cm-7.54 mS/cm (Figure 4.5). According to Luxan's classification of pozzolanicity (Luxan et al. 1989), the changes in electrical conductivity of calcium hydroxide solution before and after addition of pozzolanic material are classified as; good pozzolana when more than 1.2 mS/cm, variably pozzolana when 1.2 - 0.4 mS/cm and non-pozzolanic when less than 0.4 mS/cm. Measurement results in this study concluded that except for the H-M-BB sample, all aggregates could be classified as good pozzolana. These pozzolanic activity values, except of the Ç-M-SS, Ç-M-BB3 and H-M-BB samples, were higher than the pozzolanic activity values of aggregates that were used in Anatolian Seljuk Buildings (Tuncoku 2001).



	Ç-M-BB1	Ç-M-BB2	Ç-M-SS	Ç-P	Ç-P2	Ç-M-BB3	H-M-BB	H-M-SS
■ Pozzolanic activity(mS/cm)	5,37	5,67	2,71	7,54	7,47	2,71	1,71	7,23

Figure 4.5. Pozzolanic activity values of fine aggregates (<53 μm)

Pozzolanic aggregates react with lime and produce amorphous silicates and aluminates, which are the products that give the mortar the ability of hardening under water (Charola et. al. 1999, Palomo et al. 2002). Usage of pozzolanic aggregates in mortars of Çukur Hamam and Hacet Mescidi, improves the possibility of these mortars to be hydraulic.

4.1.6 Mineralogical, Chemical and Microstructural Properties of White Lump Samples

The paste in old mortars is inhomogeneous. It contains lime lumps, with physical and chemical properties that differ from the matrix paste. These lumps should have been formed during different stages of binder production. (Lindqvist et al. 2000).

White lump in the mortar samples are generally rounded, porous and appearing distinctly in the mortar matrix (Figure 4.6). The presence of well rounded porous white lumps indicate that the lime used was dry-slaked, that was slaked with sufficient amount of water to convert all CaO to $Ca(OH)_2$ (Elsen et al. 2004).

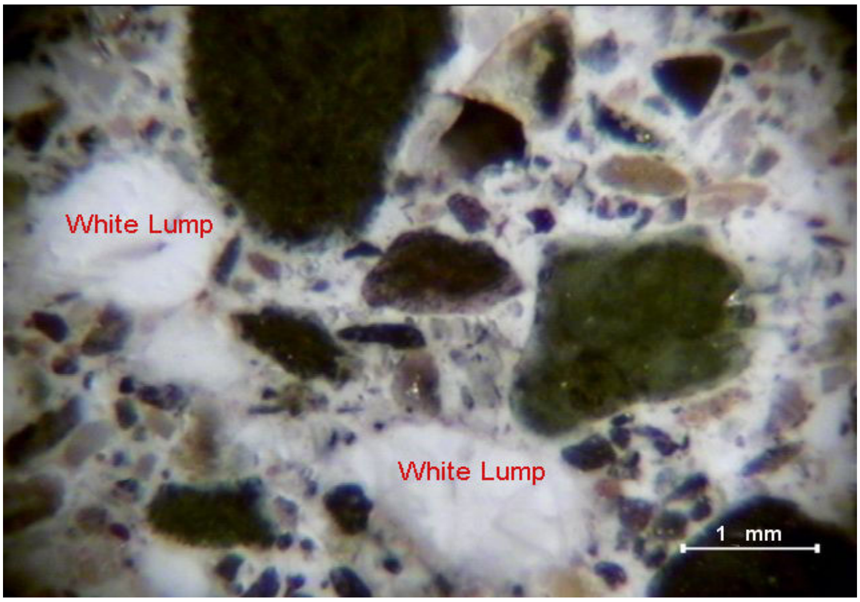


Figure 4.6. Stereo microscope image of a cross section from a stone masonry mortar sample showing the white lumps.

The presence of lumps in the mixture is probably due to insufficient mixing of lime and aggregates (Bakolas et al. 1995).

White lumps in mortar samples were characterized by XRD and SEM-EDS analysis. XRD analysis showed that the Ç-M-SS, and H-M-SS white lump samples composed only of calcite ($CaCO_3$) (Figure 4.7), and Ç-M-BB2, Ç-M-BB3 and H-M-BB samples also contain some quartz (SiO_2) in addition to calcite (Figure 4.8). Semi quantitative SEM- EDS analysis revealed that the calcium oxide (CaO) content of samples ranged between 66%-81%, silicon dioxide (SiO_2) content ranged between 8%-25%, Al_2O_3 content ranged between 2%-4% while in addition there was also little MgO, Fe_2O_3, TiO_2, Na_2O and K_2O (Table 4.2). High proportions of silicon dioxide (SiO_2) in the white lumps could be the proof of the use of siliceous limestone for the production of lime. The presence of silicon dioxide in the white lumps could not be observed in the XRD analysis of Ç-M-SS, Ç-P, Ç-P2 and H-M-SS samples. This might be due to the fact that silicon dioxide (SiO_2) present in the samples were in amorphous state.

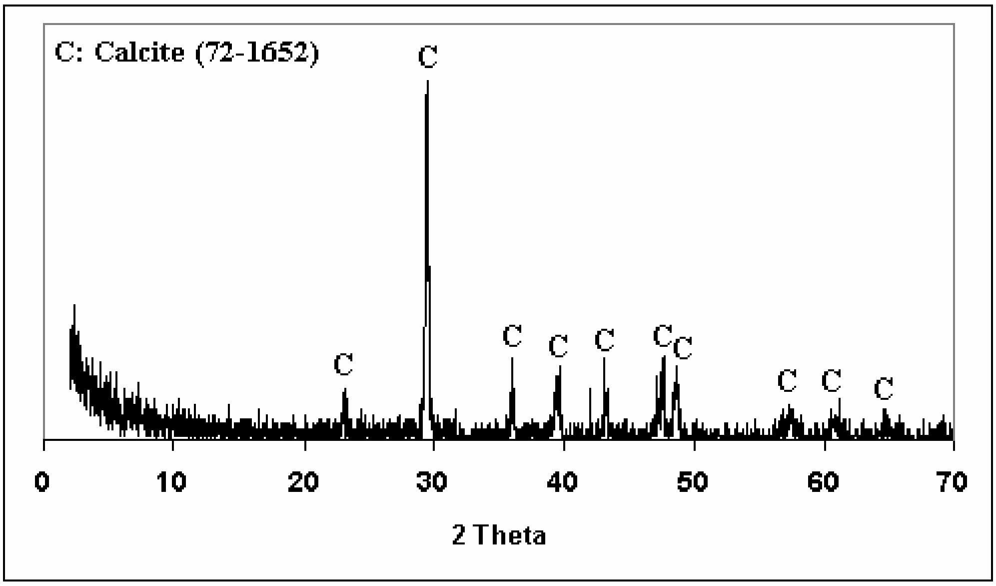


Figure 4.7. XRD pattern of white lump composed of calcite ($CaCO_3$) (Ç-M-SS)

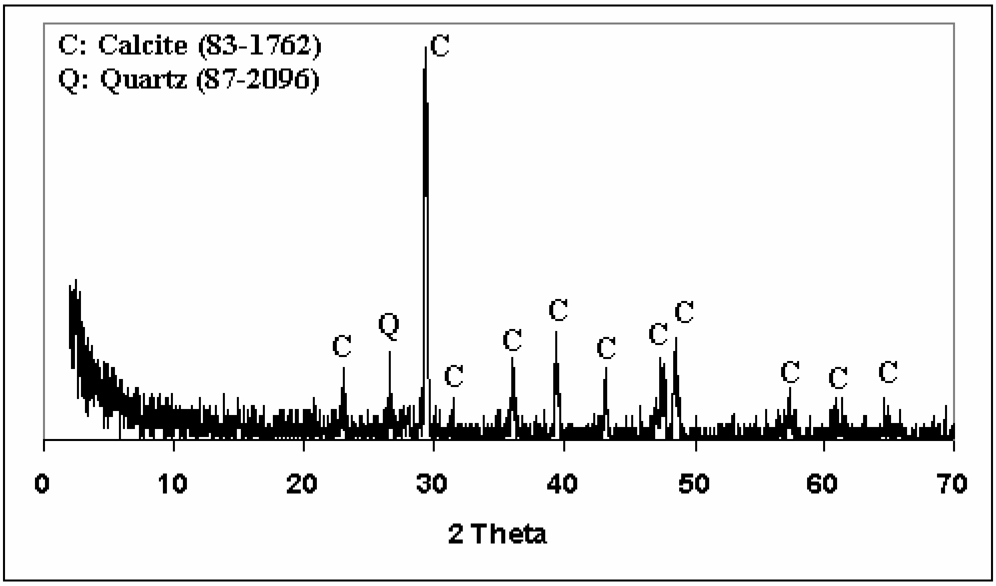


Figure 4.8. XRD pattern of white lump of composed of calcite ($Ca(CO)_3$) and quartz (SiO_2) (H-M-BB)

Table 4.2. Chemical composition of white lump samples (EDS)

Oxide (%)	**Ç-M-BB2**	**Ç-M-SS**	**Ç-M-BB3**	**H-M-BB**	**H-M-SS**
CaO	76	81	74	66	76
MgO	3	6	3	3	3
SiO_2	16	8	16	25	16
Al_2O_3	3	2	4	4	2
Fe_2O_3	1	1	2	1	1
Na_2O	1	1	1	1	1
K_2O	1	1	1	1	1

4.1.7 Mineralogical Properties of Mortar Samples

XRD analyses of the matrix was performed in order to see whether there was any C-S-H (calcium silicate hydrate) crystals and other new formations in the binder and aggregate mixture. Mortars were composed of calcite, due to carbonation of lime, and quartz and albite minerals from aggregates (Figure 4.9-Figure 4.13). No peaks were observed for hydraulic reaction products of C-S-H because their peaks coincide with the main calcite peaks.

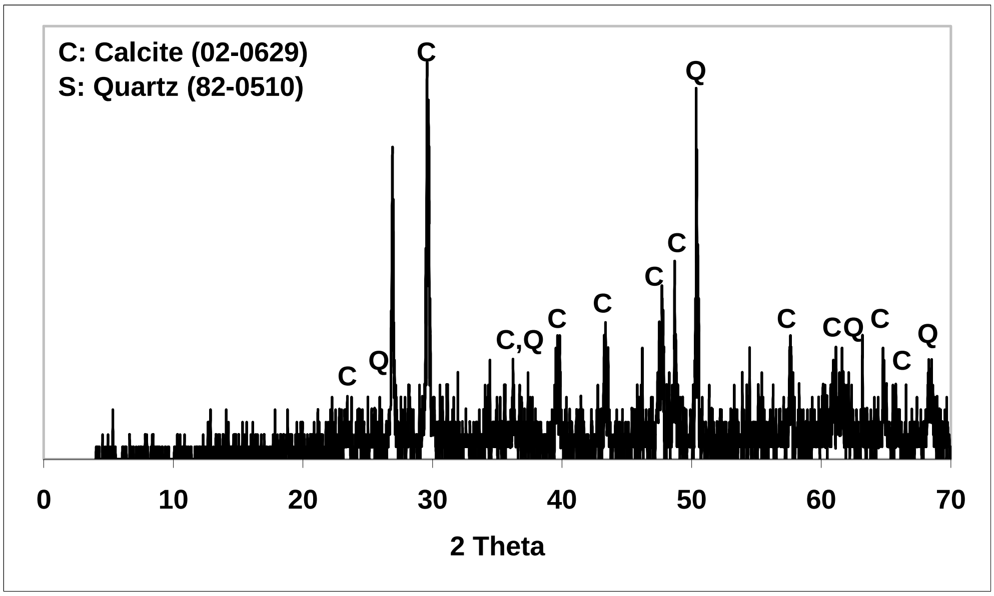


Figure 4.9. XRD pattern of mortar sample (Ç-M-BB1)

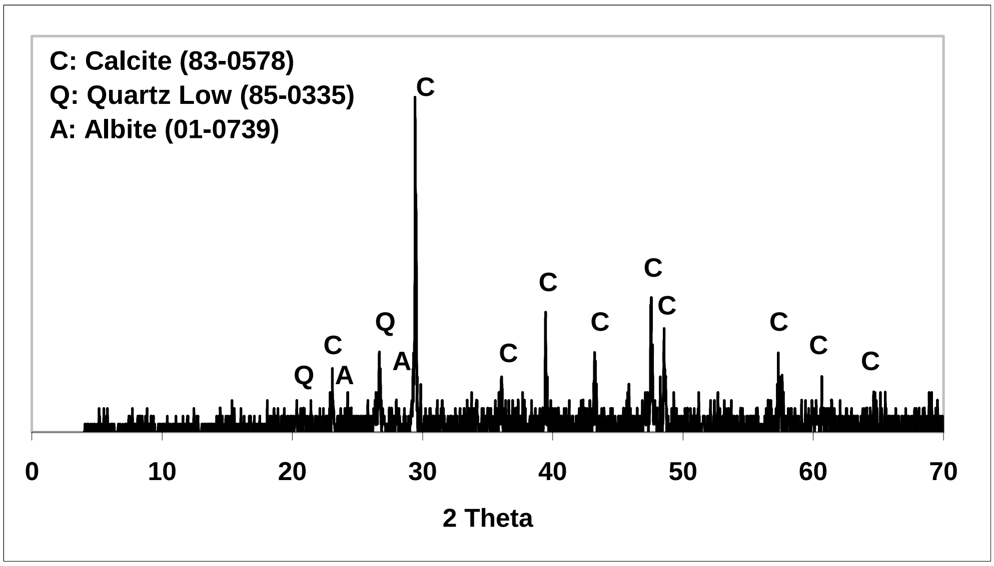


Figure 4.10. XRD pattern of mortar sample (Ç-M-BB2)

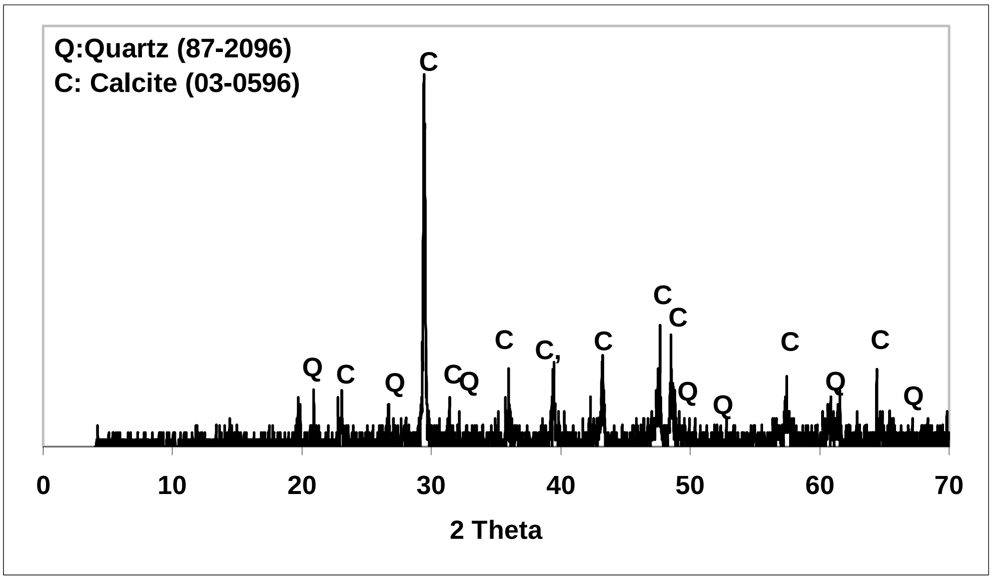


Figure 4.11. XRD pattern of mortar sample (Ç-M-SS)

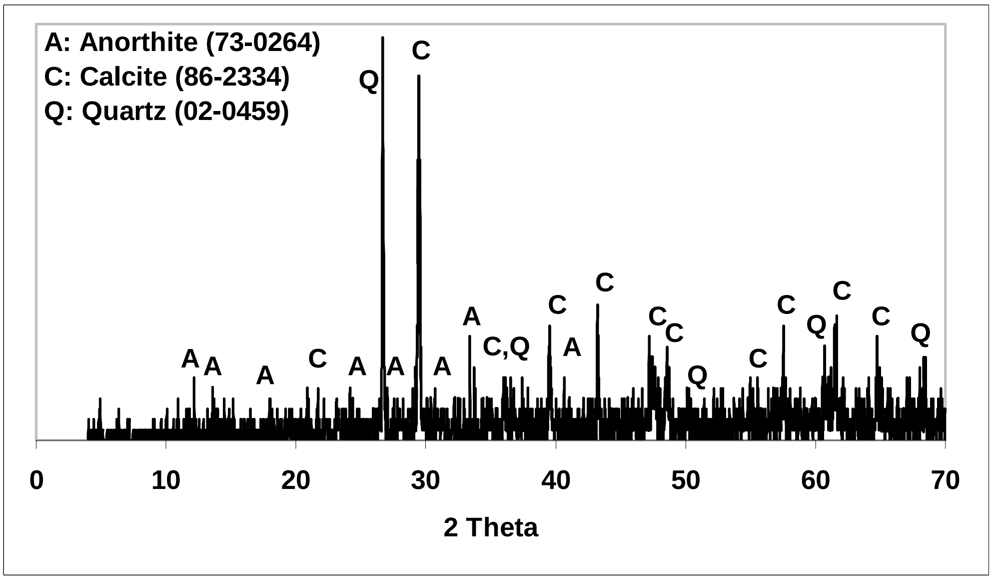


Figure 4.12. XRD pattern of mortar sample (H-M-BB)

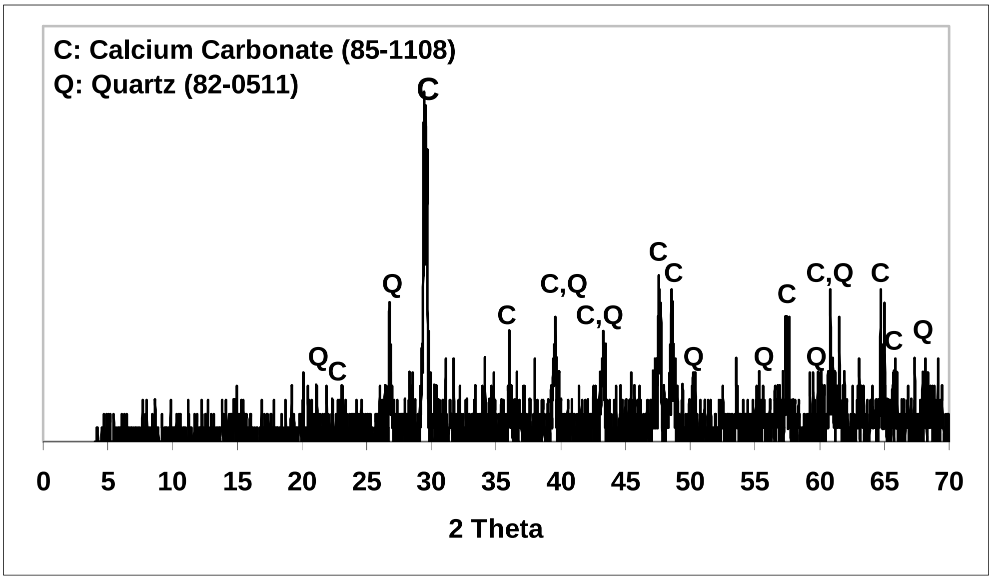


Figure 4.13. XRD pattern of mortar sample (H-M-SS)

4.1.8 Microscopic (OP-SEM) Characterization of Mortar Samples

Mortar and brick samples had aggregates, which were firmly embedded in the structure (Figure 4.14-Figure 4.19). Mixing process and the composition of aggregates have importance on the strength of the mortar and brick samples. When aggregates with a correct shape, particle size distribution, and chemical property are properly mixed with lime, it will provide good adhesion with lime and hence improve the strength properties of mortar and brick.

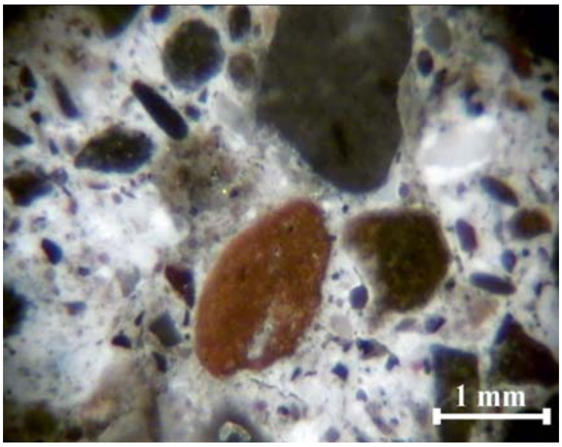


Figure 4.14. Stereo microscope image of H-M-SS

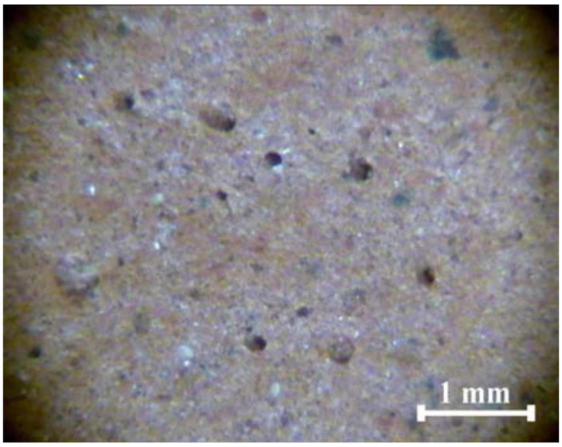


Figure 4.15. Stereo microscope image of Ç-B

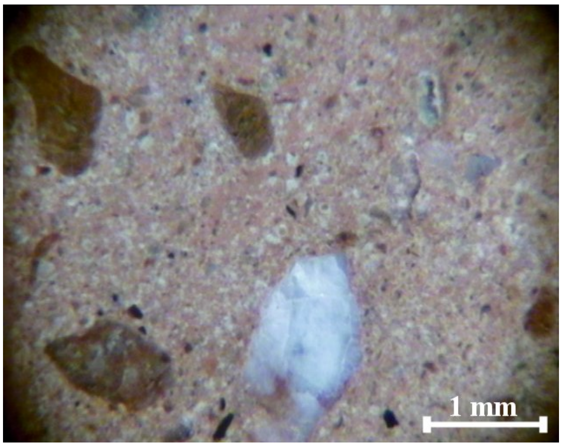


Figure 4.16. Stereo microscope image of H-B

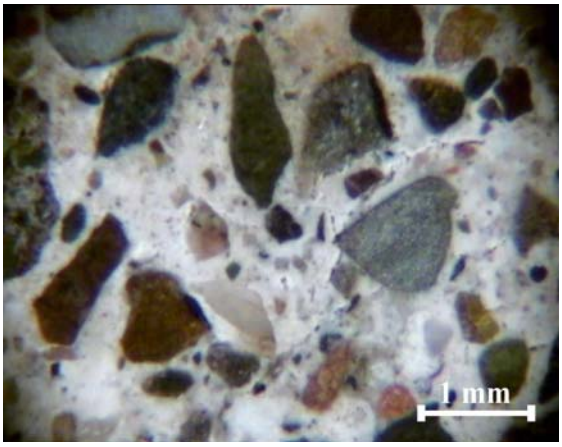


Figure 4.17. Stereo microscope image of Ç-M-SS

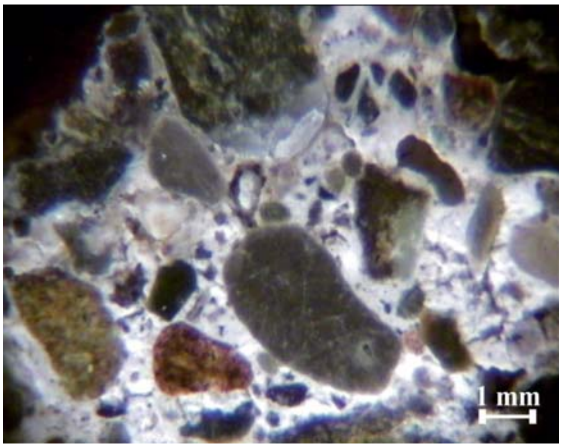


Figure 4.18. Stereo microscope image of Ç-M-BB3

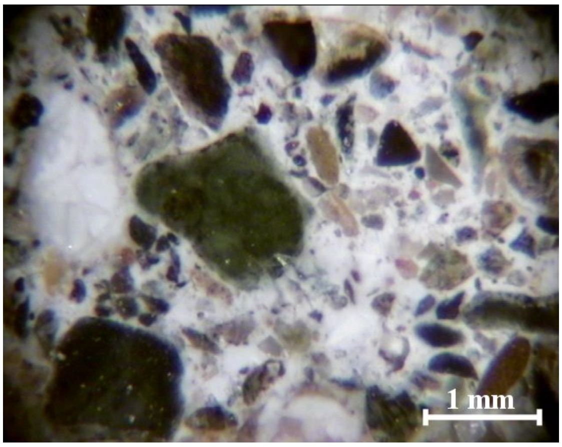


Figure 4.19. Stereo microscope image of H-M-BB

Good adhesion of aggregates with lime and brick can be seen in backscattered electron image (BSE) of the samples (Figure 4.20-Figure 4.24). The advantage of BSE observation in SEM is that it enables better distinction of chemical differences throughout the specimen surface. Features like fine cracks in aggregate (Figure 4.20) or in the mortar (Figure 4.24) were observed. The latter showed an example for the degree of tolerating the stresses and strains that may occur in masonry during use (Davison 1976).

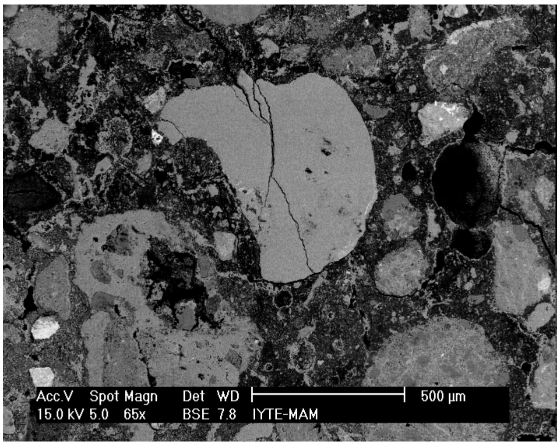


Figure 4.20. BSE (Back Scattered Electron) image of H-M-SS

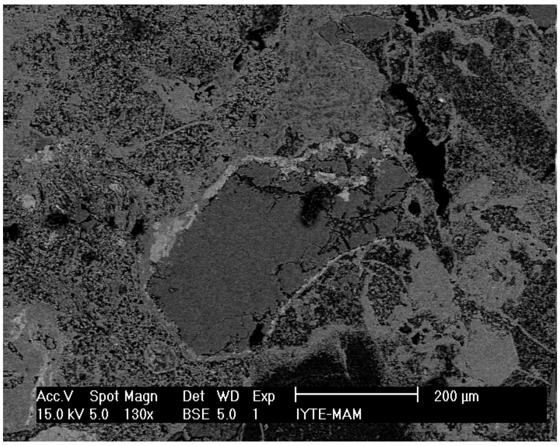


Figure 4.21. BSE (Back Scattered Electron) image of H-M-BB

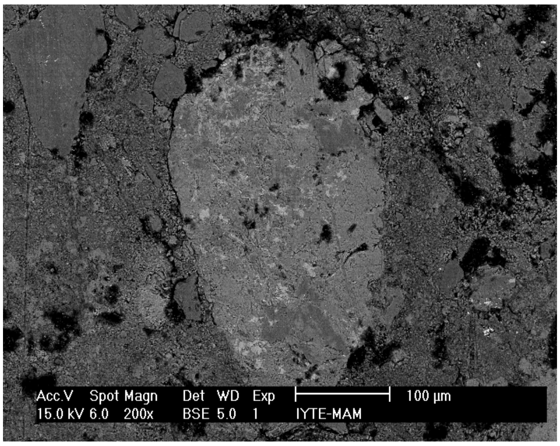


Figure 4.22. BSE (Back Scattered Electron) image of Ç-M-BB3

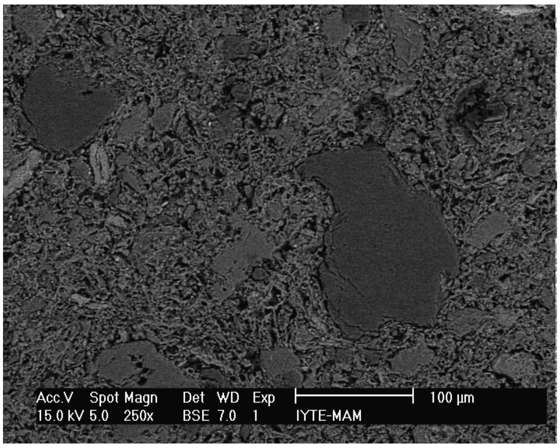


Figure 4.23. BSE (Back Scattered Electron) image of H-B

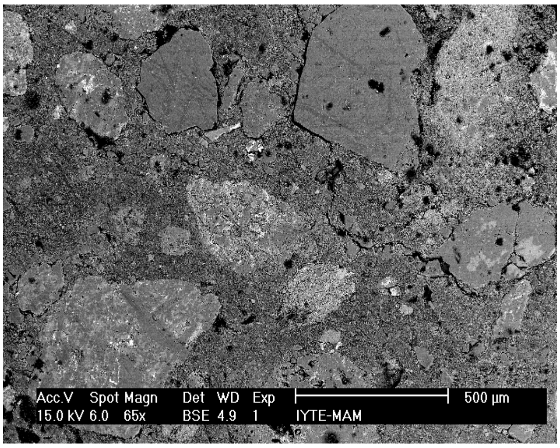


Figure 4.24. BSE (Back Scattered Electron) image of Ç-M-BB3 (with fine cracks)

4.1.9 Mineralogical, Chemical and Microstructural Properties of Aggregates

The mineralogical, chemical, and microstructural properties of fine (<53 μm) and coarse (>1180 μm) aggregates are presented in this part.

4.1.9.1 Mineralogical, Chemical and Microstructural Properties of Coarse Aggregates

The XRD analyses of coarse aggregates (>1180μm) showed that they were composed of quartz, albite and sodium aluminum silicate (Figure 4.25-Figure 4.30). The broad band in the XRD chart, indicative of the presence of amorphous materials (Sujeong 1999), could not be observed between 20-30^o in the samples. Therefore, it can be said that there was not a significant amount of amorphous materials in the structure of coarse aggregates.

Semi quantitative SEM-EDS analysis results given in Table 4.3 revealed that the main component in coarse aggregates was SiO_2, which varied in the range of 68-81%. The second components of the coarse aggregates were aluminum oxide (Al_2O_3) varied in the range of 8-10%, and the third important component was iron oxide (Fe_2O_3) which varied in the range of 3-7%. The small amounts of calcium oxide fractions in the aggregates estimated to be from the acid insoluble silicates, or the undissolved calcite.

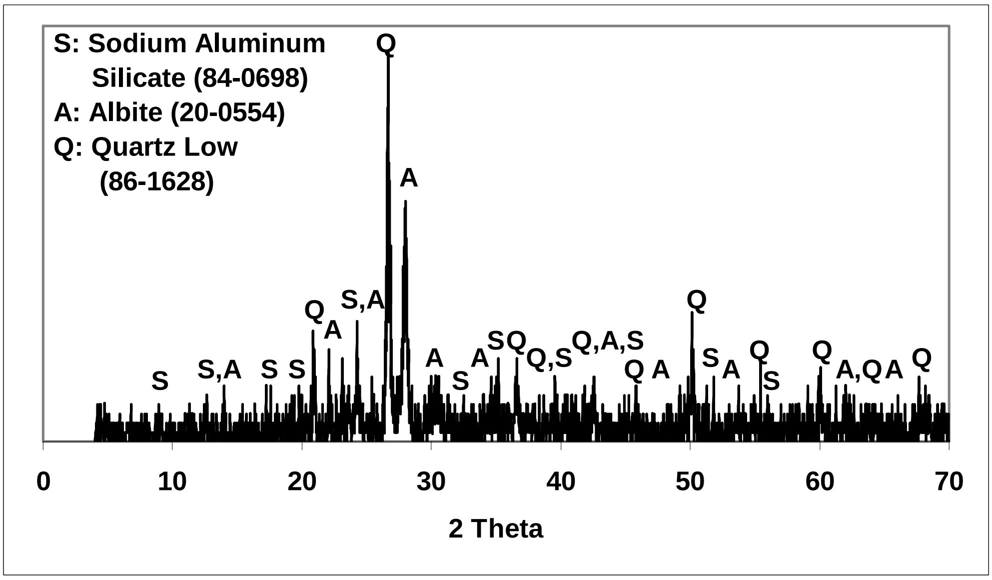


Figure 4.25. XRD pattern of the coarse aggregates used in brick masonry mortar of Ç-M-BB1

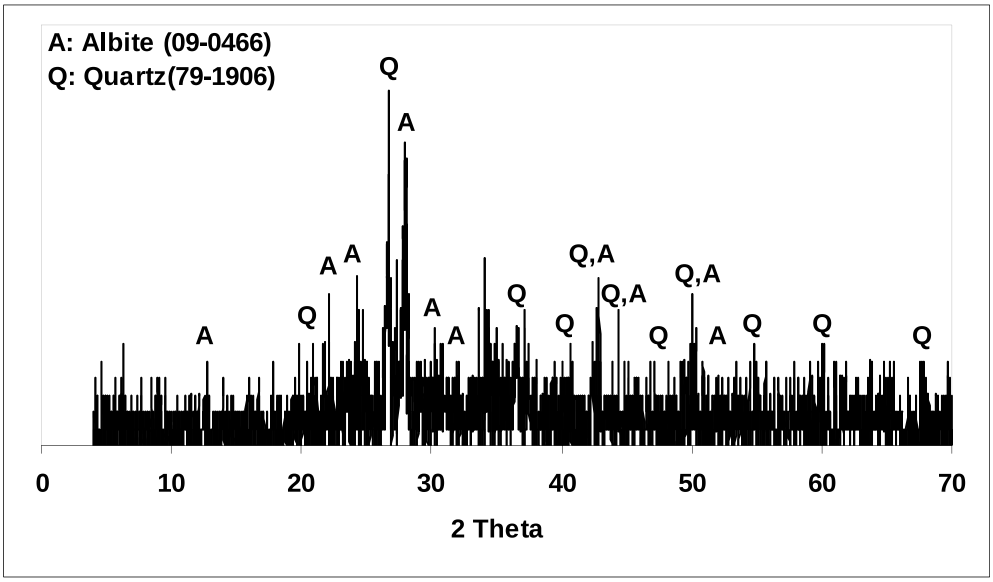


Figure 4.26. XRD pattern of the coarse aggregates used in brick masonry mortar of Ç-M-BB2

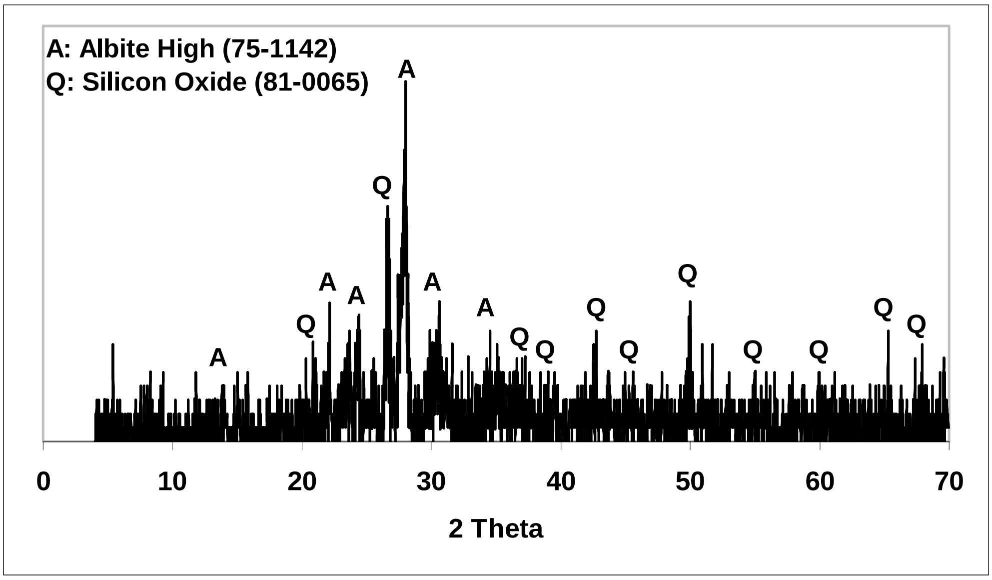


Figure 4.27. XRD pattern of the coarse aggregates used in brick masonry mortar of Ç-M-SS

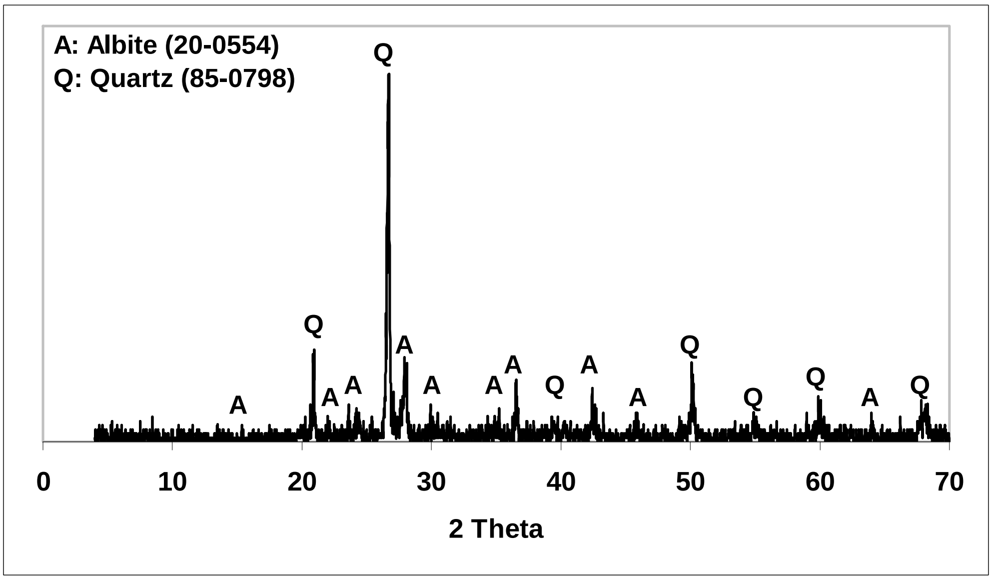


Figure 4.28. XRD pattern of the coarse aggregates used in brick masonry mortar of Ç-M-BB3

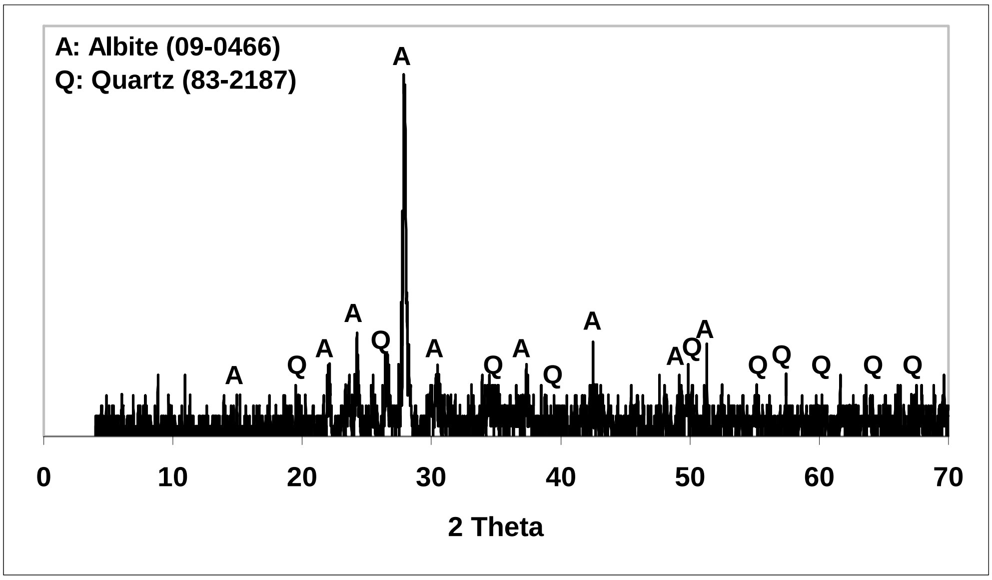


Figure 4.29. XRD pattern of the coarse aggregates used in brick masonry mortar of H-M-BB

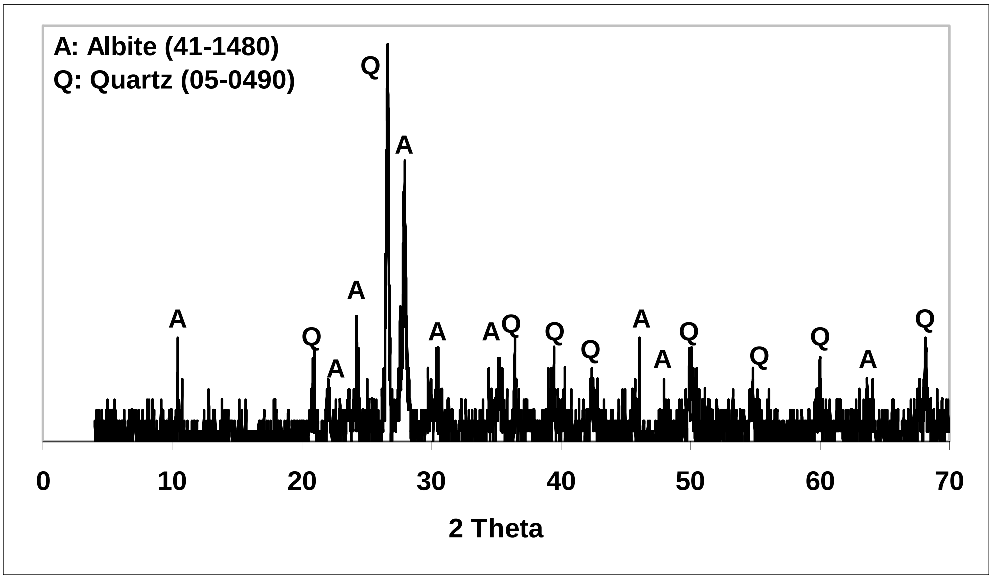


Figure 4.30. XRD pattern of the coarse aggregates used in brick masonry mortar of H-M-SS

Table 4.3. Chemical composition of coarse aggregates (EDS)

Oxide(%)	Ç-M-BB1	Ç-M-BB2	Ç-M-SS	Ç-M-BB3	H-M-BB	H-M-SS
CaO	4	4	4	2	5	4
MgO	3	4	3	3	2	2
SiO_2	74	68	72	81	72	74
Al_2O_3	10	10	9	8	10	8
Fe_2O_3	3	7	3	3	4	5
Na_2O	2	2	2	1	3	3
K_2O	3	3	4	2	2	2
TiO_2	2	2	2	1	3	3

The coarse aggregate crystals were rounded in shape (Figure 4.31). Rounded shape reduces surface area of coarse aggregates and with decrease in surface area the pozzolanic reaction between coarse aggregates and lime decreases.

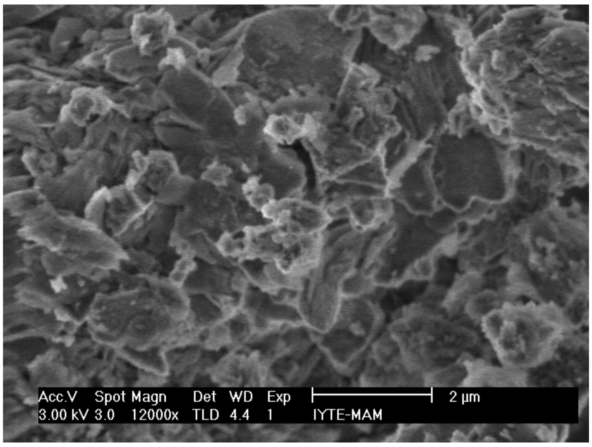


Figure 4.31. BSE (Back Scattered Electron) image of coarse aggregates

4.1.9.2 Mineralogical, Chemical and Microstructural Properties of Fine Aggregates

The XRD analyses of fine aggregates showed that they were all composed of quartz and some albite, anorthite or muscovite (Figure 4.32-Figure 4.35). The broad band indicating the presence of amorphous materials (Sujeong 1999) could be observed between 20-30° in XRD patterns (Figure 4.33-Figure 4.34- Figure 4.35). Therefore, it can be said that there is amorphous materials in the structure of fine aggregates

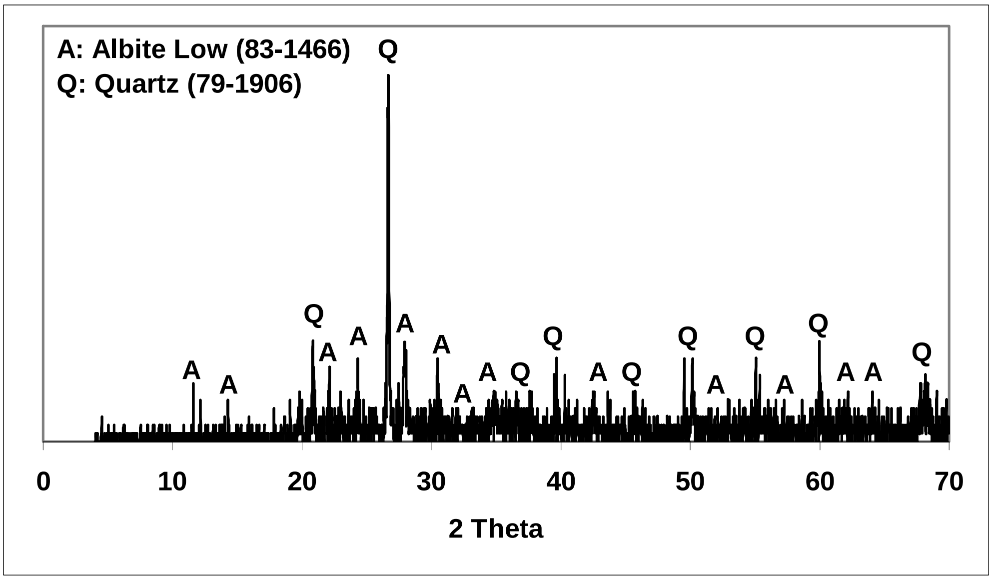


Figure 4.32. XRD pattern of the fine aggregates used in brick masonry mortar of Ç-M-BB2

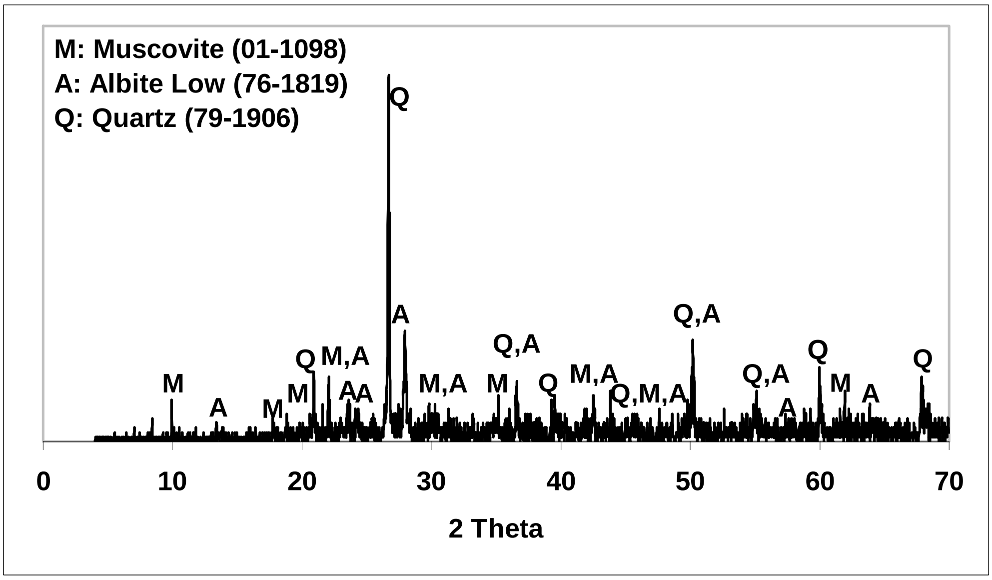


Figure 4.33. XRD pattern of the fine aggregates used in brick masonry mortar of Ç-M-SS

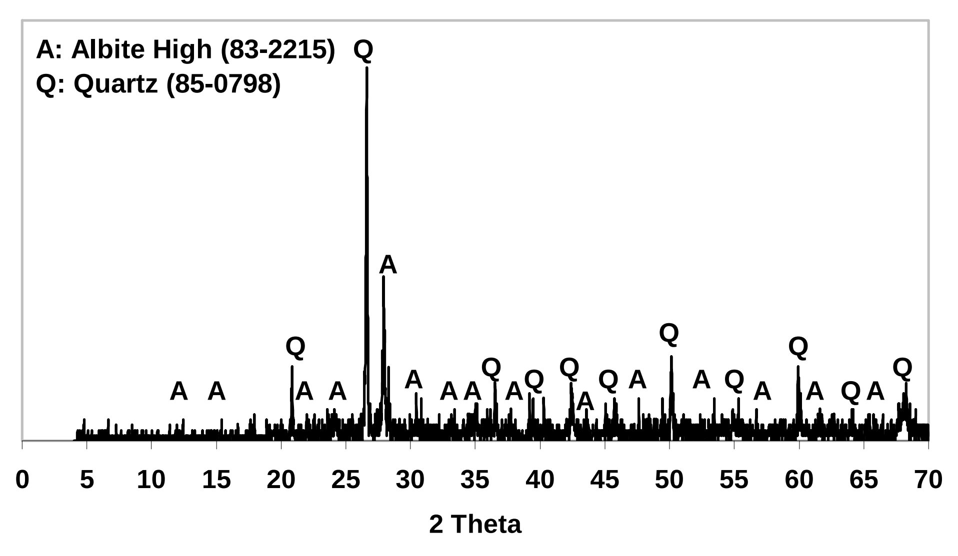


Figure 4.34. XRD pattern of the fine aggregates used in brick masonry mortar of Ç-M-BB3

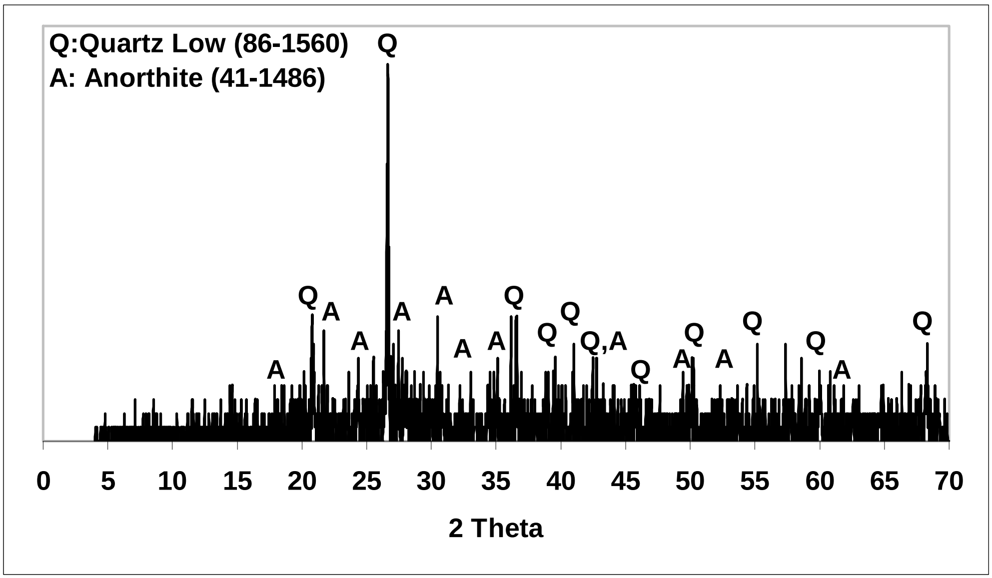


Figure 4.35. XRD pattern of the fine aggregates used in brick masonry mortar of H-M-SS

Semi quantitative SEM-EDS analysis results, in the form of oxide compositions, revealed that the main component in fine aggregates was Si, which varied in the range of 73-85% (SiO_2) (Table 4.4). The second component of coarse aggregates was aluminum that varied in the range of 6-10% (Al_2O_3), and the third important component was iron which varied in the range of 1-3% (Fe_2O_3). The small amounts of calcium in the aggregates were thought to originate from the acid insoluble silicates, or the undissolved calcite. High pozzolanic activity of fine aggregates can be attributed to high amount of silicon. The compositions are given in oxide form and do not necessarily mean that the particular oxide form is present.

Table 4.4. Chemical composition of fine aggregates (EDS)

Oxide(%)	Ç-M-BB2	Ç-M-SS	Ç-M-BB3	H-M-SS
CaO	2	2	3	2
MgO	3	2	3	3
SiO_2	76	85	73	81
Al_2O_3	10	6	10	8
Fe_2O_3	3	1	1	2
Na_2O	3	2	4	2
K_2O	2	1	3	2
TiO_2	1	1	1	1

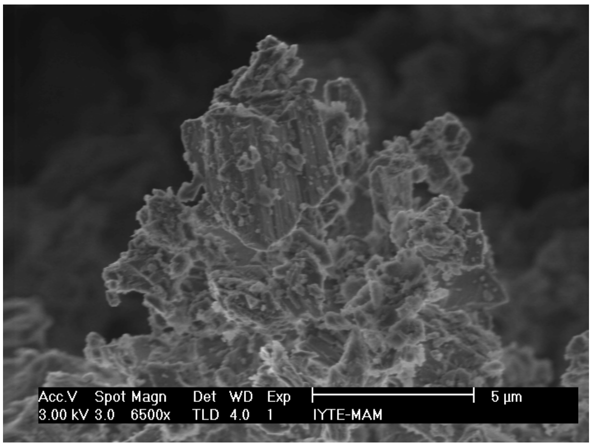


Figure 4.36. BSE (Back Scattered Electron) image of fine aggregates

The crystals of fine aggregates had sharp edges (Figure 4.36) that cause high surface area which is effective for pozzolanic reaction kinetics between lime and fine aggregate. Fine aggregates adhere to mortar matrix via pozzolanic reaction products, which improves the mechanical strength of mortar.

4.1.10 TGA Analyses of Mortar Samples

Thermal analysis has been performed in order to gain further insight of the nature of mortars. The temperature ranges at which weight loss occurs provides characterization data for ancient mortars. For example, weight loss due to adsorbed water occurs around <120°C (Alvarez et al. 2000, Bakolas et. al 1998, Ingo et. al. 2004) when there are not particular hydrated salts. The loss of chemical water bound to the several calcium aluminum silicate hydrates (CSH, CAH, CASH) occurs around 200-600°C (Ingo et. al 2004, Bakolas et. al 1998, Moroupolu 2000, Moroupolu et. al. 2003). The loss of CO_2 due to decomposition of carbonates takes place at >600°C (Bakolas et. al. 1998, Moroupolou 2000, Alvarez et al. 2000, Moroupolou et. al. 1995).

Table 4.5. TGA analyses results of the plaster and mortar samples

	Weight Loss per Temperature Range (%)			
Samples	**<120**	**120-200°C**	**200-600°C**	**>600°C**
Ç-M-BB1	0.1	0.3	2.1	10.0
Ç-M-BB2	0.8	0.3	2.2	12.7
Ç-M-SS	0	0.1	2.2	16.1
Ç-P	1.2	0.6	3.7	22.0
Ç-M-BB3	0	0.1	1.9	11.9
H-M-BB	0.6	0.6	2.5	12.7
H-M-SS	0	0.5	2.5	14.2

Brick masonry mortar samples of Ç-M-BB1, Ç-M-BB2, Ç-M-BB3, H-M-BB contained 10-12.7 % CO_2 and 1.9-2.5 % chemical water (Table 4.5-Table 4.6, Figure 4.37). Their CO_2/H_2O ratios were below 10 (Table 4.6). Therefore, these brick masonry mortars can be classified as hydraulic mortar (Moroupolou 2000). Stone masonry mortar samples of Ç-M-SS and H-M-SS contained 14.2-16.1% CO_2 and 2.2-2.5 % H_2O (chemical water) (Table 4.5-Table 4.6, Figure 4.37) and their CO_2/H_2O ratios were below 10 (Table 4.6). Therefore, these stone masonry mortars can also be classified as hydraulic mortar.

Table 4.6. Structurally bound water (H_2O) percent, carbondioxide percent (CO_2) and CO_2/H_2O ratio of mortar and plaster samples

Samples	**CO_2**	**H_2O**	**CO_2/H_2O**
Ç-M-BB1	10.0	2.1	4.76
Ç-M-BB2	12.7	2.2	5.77
Ç-M-SS	16.1	2.2	7.31
Ç-P	22.0	3.7	5,94
Ç-M-BB3	11.9	1.9	6.26
H-M-BB	12.7	2.5	5.08
H-M-SS	14.2	2.5	5.68

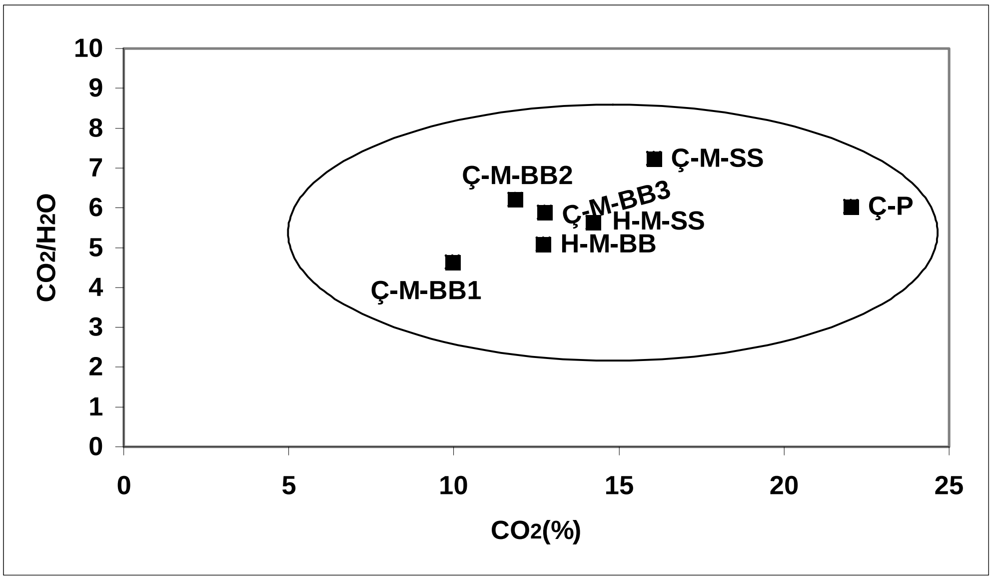
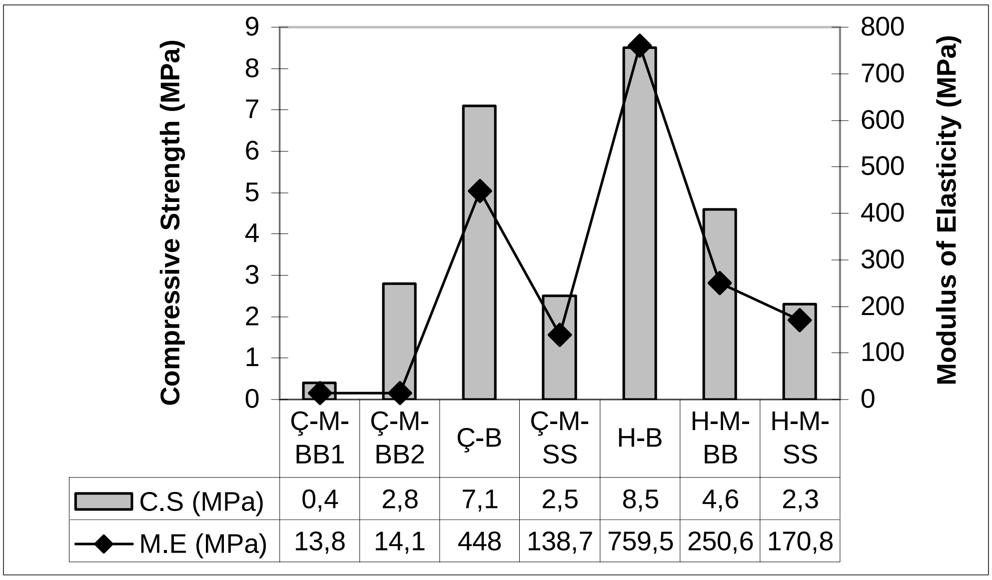


Figure 4.37. Inverse hydraulicity (CO_2/H_2O) versus CO_2 % of brick masonry and stone masonry mortars

4.1.11 Mechanical Properties of Mortar and Brick Samples

The strength and elasticity values have been used for evaluation of mechanical properties of the mortar and brick samples. Strength values were in the range of 0.4-4.6 MPa for mortar samples and between 7.1-8.5 MPa for brick samples (Figure 4.38). Modulus of elasticity values of mortars samples were in the range of 13.8-250.6 MPa and between 448-759.5 MPa for brick samples (Figure 4.38). Brick samples presented higher strength and elasticity values than the mortar samples.



	Ç-M-BB1	Ç-M-BB2	Ç-B	Ç-M-SS	H-B	H-M-BB	H-M-SS
▭ C.S (MPa)	0,4	2,8	7,1	2,5	8,5	4,6	2,3
◆ M.E (MPa)	13,8	14,1	448	138,7	759,5	250,6	170,8

Figure 4.38. Compressive strength and Modulus of Elasticity values of mortar and brick samples (C.S: Compressive Strength, M.E: Modulus of Elasticity)

4.2 Intervention Mortars

Repair mortars have important effect on the success of restoration process. The compatibility of repair mortar and original components is desirable (Mosquera et.al. 2002, Degryse et.al. 2002). The compatibility includes the chemical compatibility between the repointing mortar and old material, physical compatibility, with special reference to processes of solubility and of water transport, and the structural and mechanical compatibility.

There has been a tendency to replace mortars with cement based mortars in restoration of masonry structures in the first half of the 20th century. Cement based mortars have high content of soluble salt that causes damage by crystallization-hydration cycles (Rodriguez-Navarro et.al. 1998). Cement based mortars have less porosity, so it retains excess water in structure, and finally cement based mortars have higher compressive strength than the other masonry materials. Masonry structures show some degree of movement resulting from the thermal effects or creep (Mosquera et.al. 2002, Hendry 2001). Because of strong character of cement, it restrains movement and leads to stress that can cause failure. Due to incompatibilities of cement based mortars with originals extensive damage occurred in structures which have been restored by cement based mortars (Degryse et.al. 2002, Moropoulou et.al.2002, Rodriguez-Navarro et.al. 1998). Use of lime mortars in restoration gained importance, due to numerous advantages, when compared with cement. Advantages of lime based mortars are; chemical and physical compatibility with the ancient mortars due to similar composition, similar strength values with the originals and ability to accommodate movement in masonry, and the low cost of lime.

4.2.1 Characteristics of the Lime

Figure 4.39 presents the X-ray diffraction (XRD) chart of the lime, and Figure 4.40 gives the chemical analysis by EDS. Both figures showed that the lime was relatively pure.

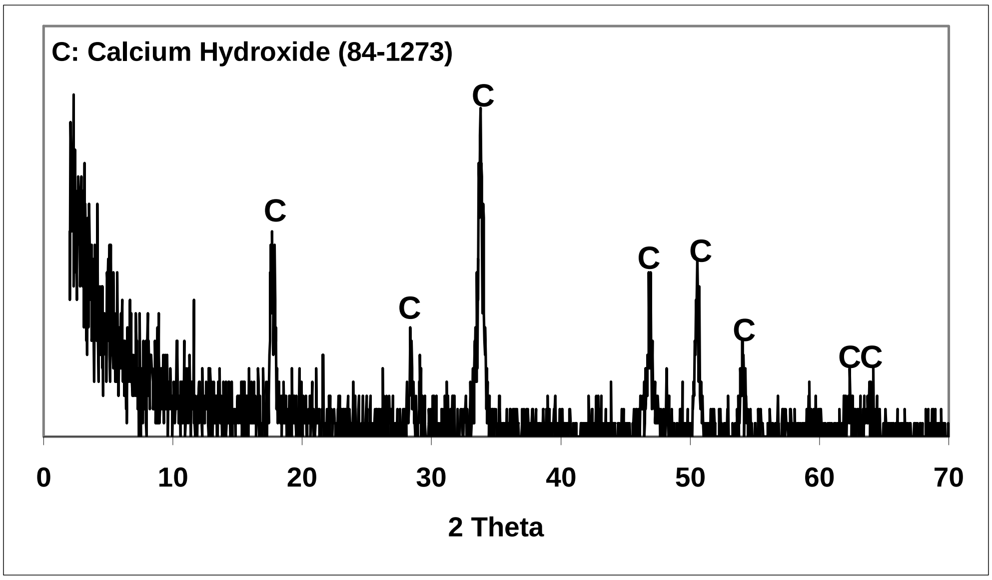
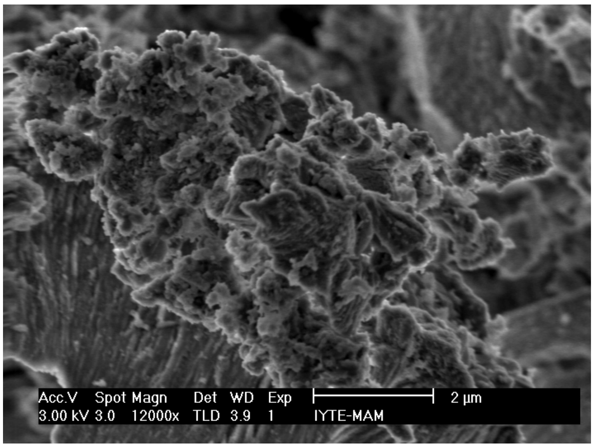


Figure 4.39. XRD pattern of commercial lime used in mortar preparation



Oxides	%
Na_2O	0.3
MgO	1.2
Al_2O_3	0.4
SiO_2	1.0
K_2O	0.5
CaO	96.3
TiO_2	0.1
Fe_2O_3	0.3

Figure 4.40. SE (secondary electron) image and chemical composition of commercial lime

4.2.2 Characteristics of the Aggregates

Sand was mainly composed of quartz and anorthite and the other compounds were present but in small amounts so couldn't be detected by XRD analysis (Figure 4.41, Table 4.7). Aggregates were made up of sand with angular edges.

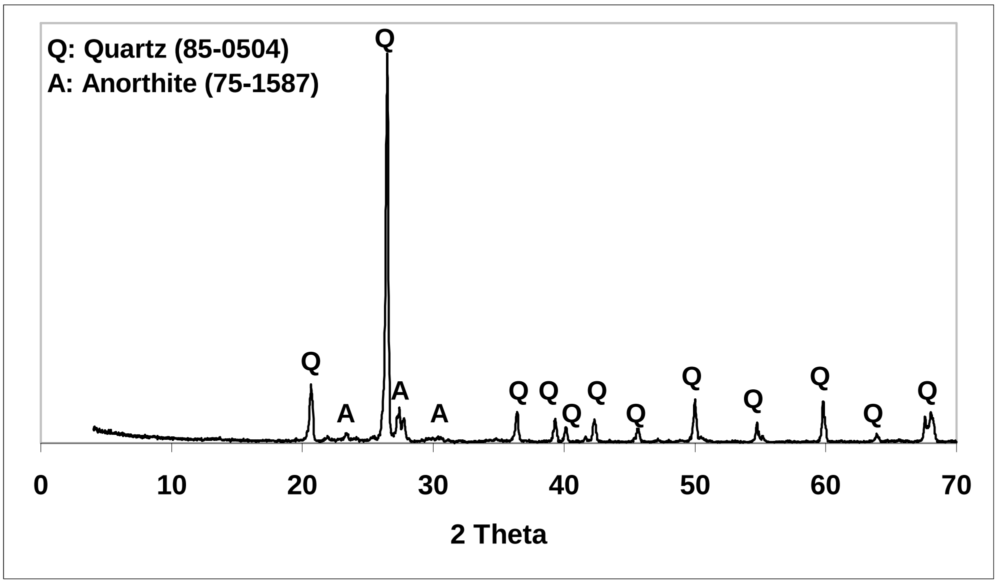


Figure 4.41. XRD pattern of commercial aggregate used in mortar preparation

Table 4.7. Chemical composition (%) of standard sand (EDS)

Oxides	**%**
Na_2O	1.5
MgO	0.9
Al_2O_3	5.4
SiO_2	86.1
K_2O	3.0
CaO	1.5
TiO_2	0.8
Fe_2O_3	0.8

4.2.3 Characteristics of the Pozzolanas

A number of possible pozzolanic aggregates can be used in making hydraulic lime mortars: low heated clay, natural pozzolanas like diatomaceous earth, amorphous silica derivatives. In this thesis, clay was chosen for a case study to see whether pozzolanicity could be obtained from industrially available non-pozzolanic ceramic clay products. The purpose was to test the hypothesis that low temperature heating of clay at T=400-900°C produces metakaolin type of amorphous phase which possesses good pozzolanic properties suitable for use in lime mortars to make them hydraulic. The end result would mean that a hydraulic lime mortar could be reproduced using locally available raw materials for potential intervention mortars for conservation purposes.

Clay in the form of low heated brick has long been used as artificial pozzolana in preparation of mortars. The characterization of clay is very important to find the suitable clay which will have the maximum pozzolanic character. The heat treatment application has important effect on pozzolanic activity of clay. The clay is composed mainly of silica and alumina. The loss of combined water in structure of clay, due to thermal treatments causes demolition of the crystal network of the clay constituents and the silica and alumina remain in disordered but unstable amorphous state (Baronia 1997). When mixed with lime and water, they can produce pozzolanic action. Therefore, the determination of temperature range where the clay turns into unstable amorphous state is very important.

For determination of the heat treatment effect on clay samples, the samples were heated in air in a box kiln at temperatures of 400, 450, 500, 550, 600, 800, 1200°C, and structural changes of clay samples at these temperatures were determined by XRD analyses (Figure 4.42-Figure 4.45).

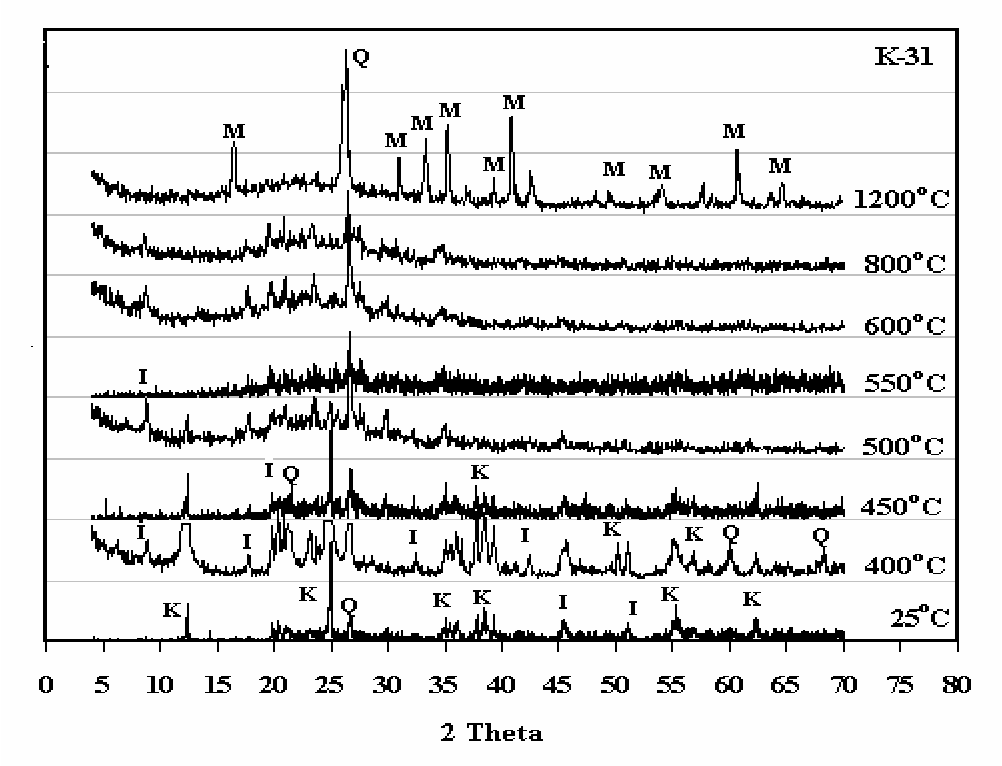


Figure 4.42. XRD analyses results of K-31 sample in the range of 25-1200°C
(K: Kaolinite, Q: Quartz, M: Mullite, I: Illite)

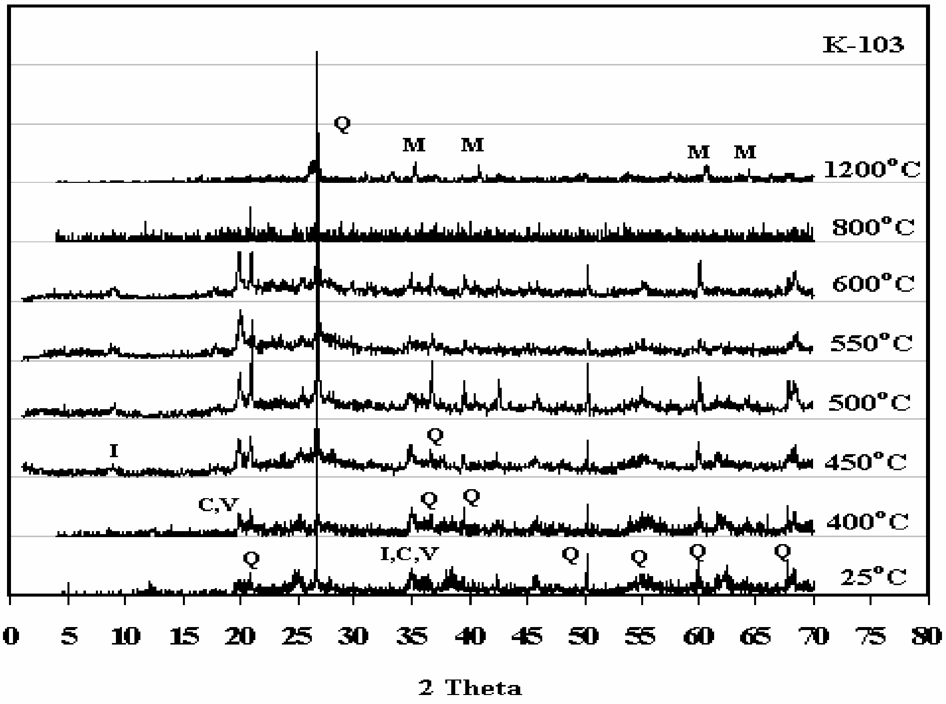


Figure 4.43. XRD analyses results of K-103 sample in the range of 25-1200°C (C: Mica, V: Muscovite, Q: Quartz, M: Mullite, I: Illite)

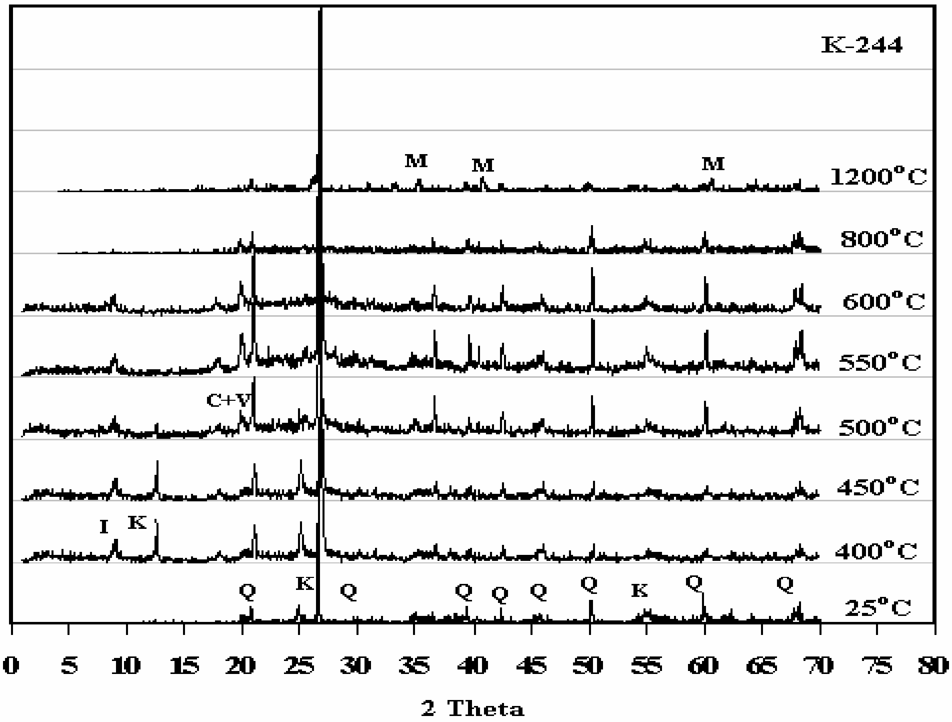


Figure 4.44. XRD analyses results of K-244 sample in the range of 25-1200°C (C: Mica, V: Muscovite, K: Kaolinite, Q: Quartz, M: Mullite, I: Illite)

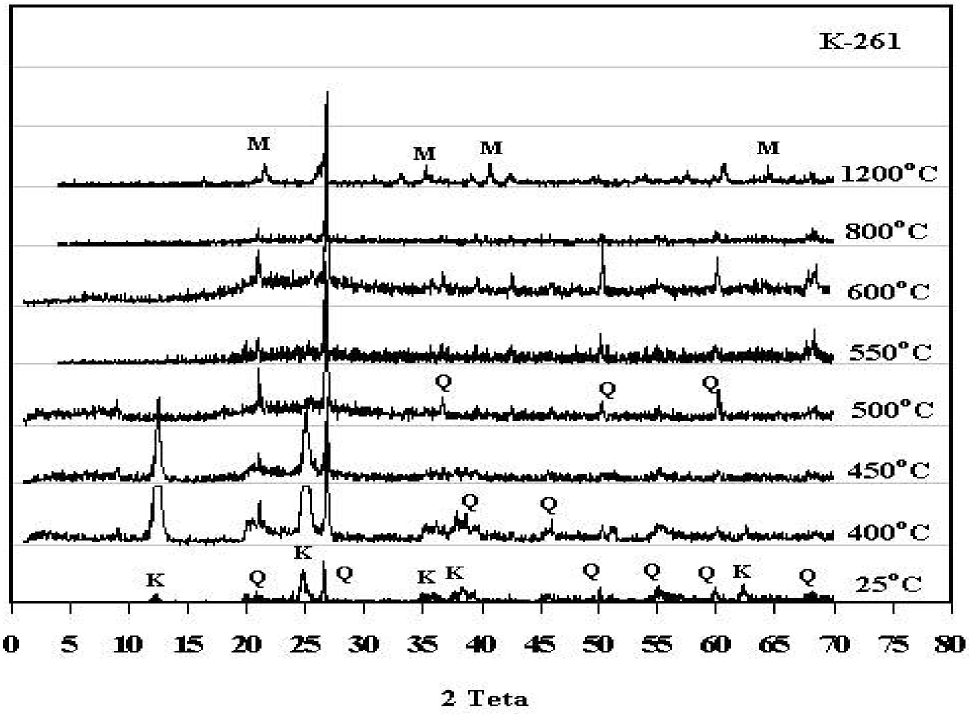
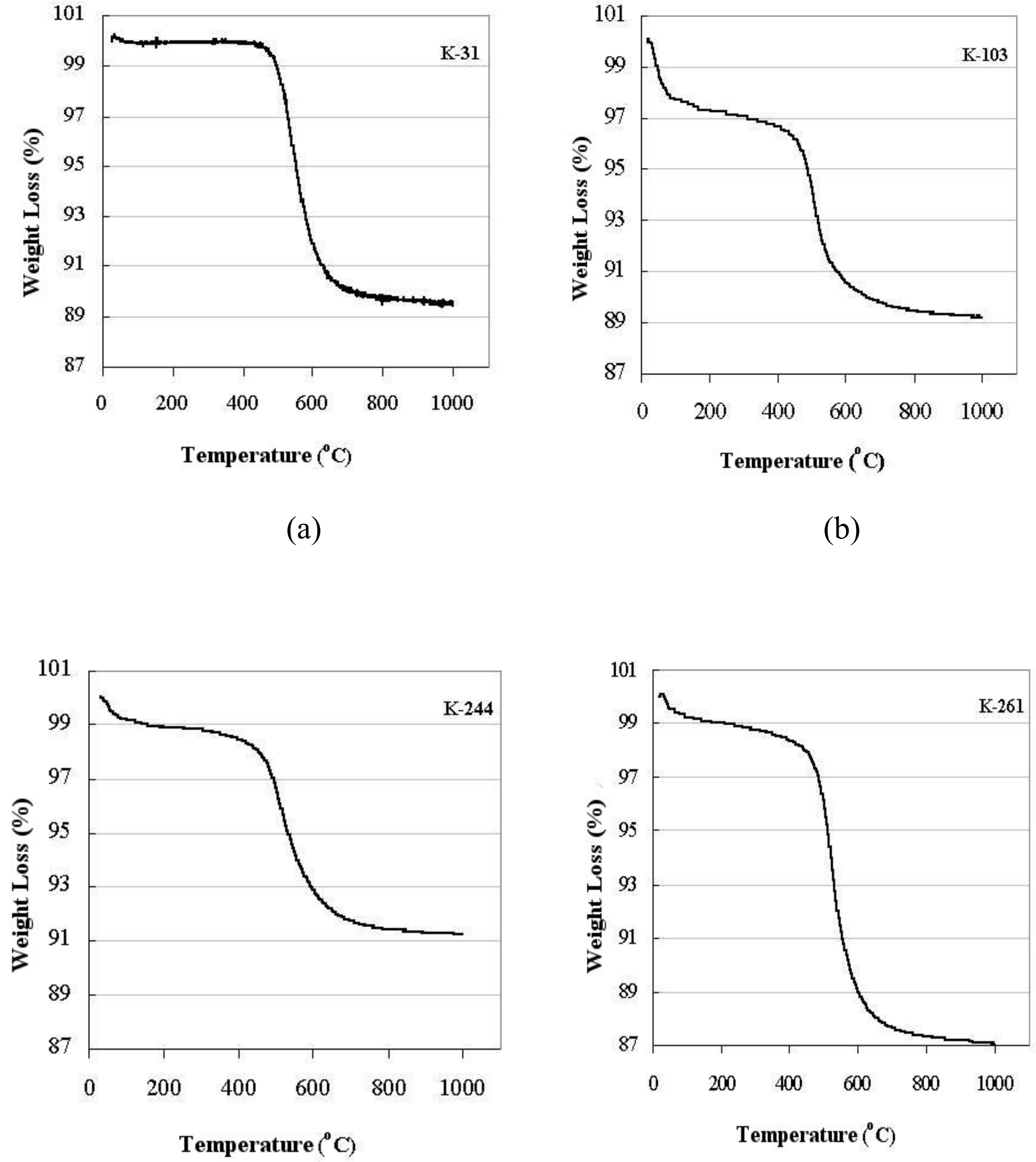


Figure 4.45. XRD analyses results of K-261 sample in the range of 25-1200°C (K: Kaolinite, Q: Quartz, M: Mullite)

Due to heat treatment, the peaks of kaolinite (K) (400-550°C), illite (I) (600-800°C), muscovite (M) and mica (C) (800-1200°C) disappeared (Figure 4.42-4.45). The broad band, which appeared in 20-30°2θ range is the evidence of the presence of the amorphous materials, that were responsible for the loss of chemical water from the structure of clay minerals (Sujeong et.al.1999). The presence of amorphous materials causes high pozzolanic activity (Sujeong et.al. 1999). The amorphous material converts to mullite mineral when the temperature exceeds 1200°C (Sujeong et.al.1999).

Thermal analyses were performed in order to gain further information about clay samples. The temperature ranges for weight loss provides information about the thermal characteristics of clay samples. These temperature ranges correspond to weight loss due to adsorbed water (25-100°C) and loss of chemical water bound to the clay minerals (400-900°C).

The weight loss corresponding to loss of chemical water for sample K-261 was 11.4% (Figure 4.46 d). The same weight losses of other samples were 10.3% for sample K-31, 8.0% for sample K-103, and 7.5% for sample K-244 (Figure 4.46 a-c). Based on these weight loss measurements, samples K-261 and K-31 were found to contain higher amount of clay minerals.



(a) (b)

(c) (d)

Figure 4.46. TGA analyses results of samples (a) K-31, (b) K-103, (c) K-244 and (d) K-261

Semi-quantitative SEM-EDS analysis showed that the clay samples had SiO_2 content ranging between 52-58%, Al_2O_3 content between 33-41%, Na_2O content between %0.9-1.2 and K_2O content between %0.4-2.6 (Table 4.8).

Table 4.8. Chemical composition (%) of clay samples (EDS)

Oxides (%)	**K-31**	**K-103**	**K-244**	**K-261**
Na_2O	0,9	0,9	1,1	1,2
MgO	1,2	1,6	1,6	1,4
Al_2O_3	41,4	33,3	33,1	40,8
SiO_2	52,6	56,5	58,7	53,4
K_2O	2,4	2,6	2,4	0,4
CaO	0,1	0,4	0,4	0,2
TiO_2	0,3	1,3	1,0	1,0
Fe_2O_3	1,1	3,4	1,6	1,6

The pozzolanic activity (PA) values of clay samples heated at different temperatures are given in Figure 4.47. It was found that most clay samples were not sufficiently pozzolanic before heat treatment. The maximum PA values were obtained for K-103 sample while the lowest PA was shown by the K-31 sample before heat treatment. High pozzolanic activity of K-103 sample can be attributed to natural pozzolanas in structure of this sample. The pozzolanic activity measurement at different temperatures showed that the maximum pozzolanic activity values for all samples were obtained in the range of 550-600 ^{o}C. This result was expected because the clay crystal structures were disrupted and an amorphous material was produced by heating at this temperature range (Sujeong et.al.1999). Pozzolanic activity values of samples decreased when this temperature range was exceeded (e.g. when T>600-800^{o}C. This fall of PA can be attributed to decreasing surface area due to heat treatment. The fall of pozzolanic activity values in the range of 800-1200^{o}C is the result of both surface area decrease and the decomposition of amorphous structures, and formation of new minerals like mullite.

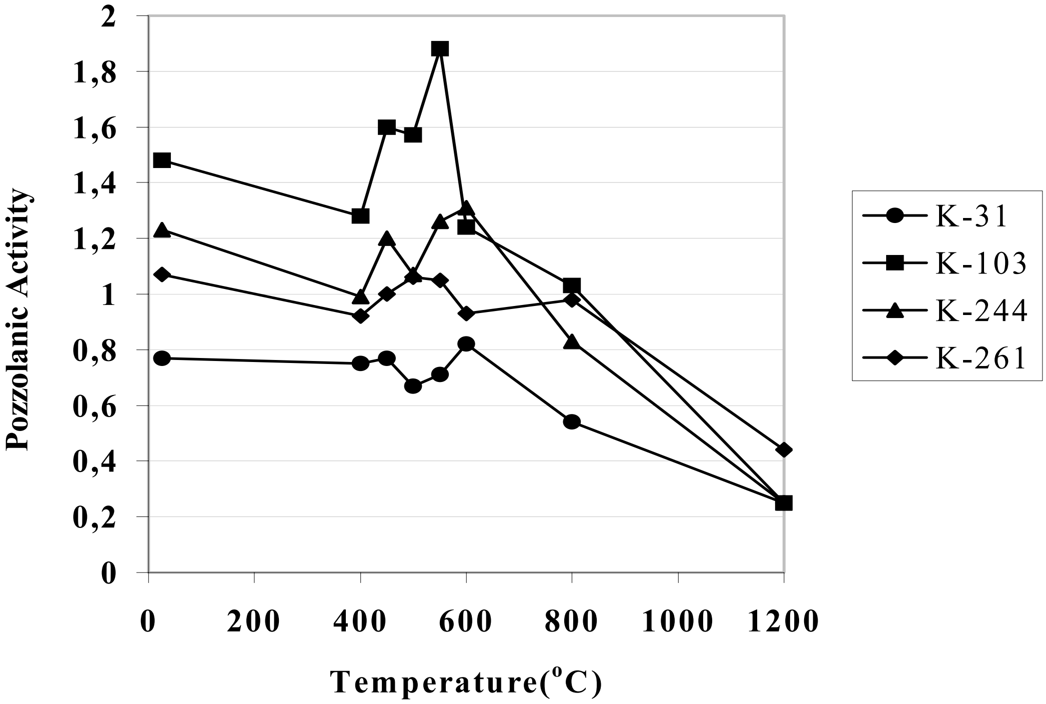


Figure 4.47. Pozzolanic activity test results of clay samples

Based on the results of XRD, TGA, EDS and PA analyses, the samples K-103 and K-244, which had broadband in 20-30° 2θ had high amount of silica (SiO_2) and alumina (Al_2O_3), combined with a high PA. Therefore, these clays were decided to be used in the production of potential intervention mortar as pozzolanic additives. The sample K-103 was used as natural pozzolana (NP) and the K-244 was used as artificial pozzolana after a heat treatment at T>500°C.

4.2.4 Carbonation of Intervention Mortars

Lime based mortars harden in two ways; during early ages, the excess water is lost and almost at the same time, the carbonation process of portlandite transforming into calcite starts. The mechanical strength increases with carbonation time. It is well known that lime mortars can take many years to reach total carbonation. The degree of mortar carbonation can be determined by XRD analysis. The results of XRD analysis after 3 months of carbonation are given in Figure 4.48-Figure 4.55.

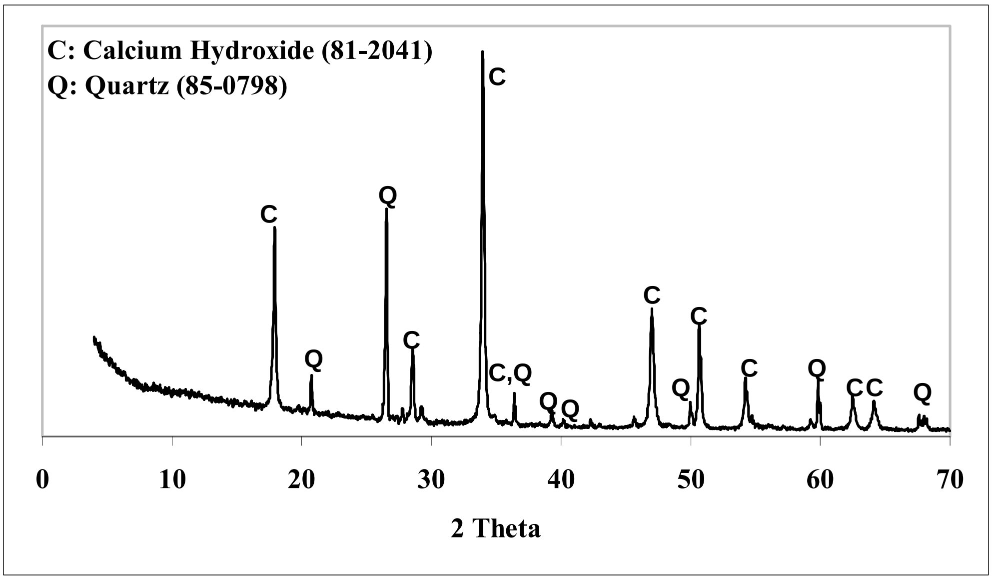


Figure 4.48. XRD analysis result of sample K-103 (NP), B/Ag Ratio 1:1 (3 months of carbonation)

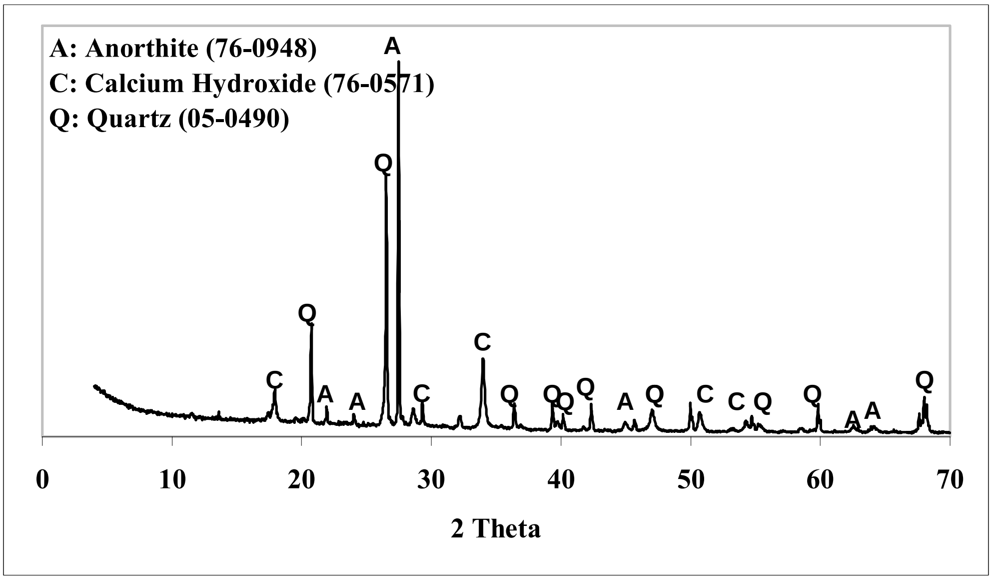


Figure 4.49. XRD analysis result of sample K244 (600 °C) B/Ag Ratio 1:1 (3 months of carbonation)

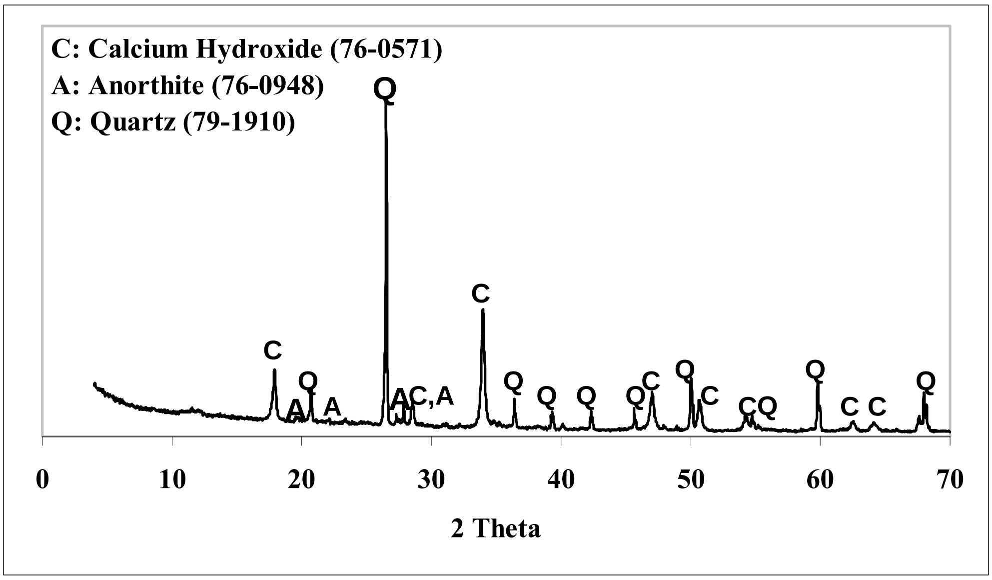


Figure 4.50. XRD analysis result of sample K-103 (NP), B/Ag ratio 1:3 (3 months of carbonation)

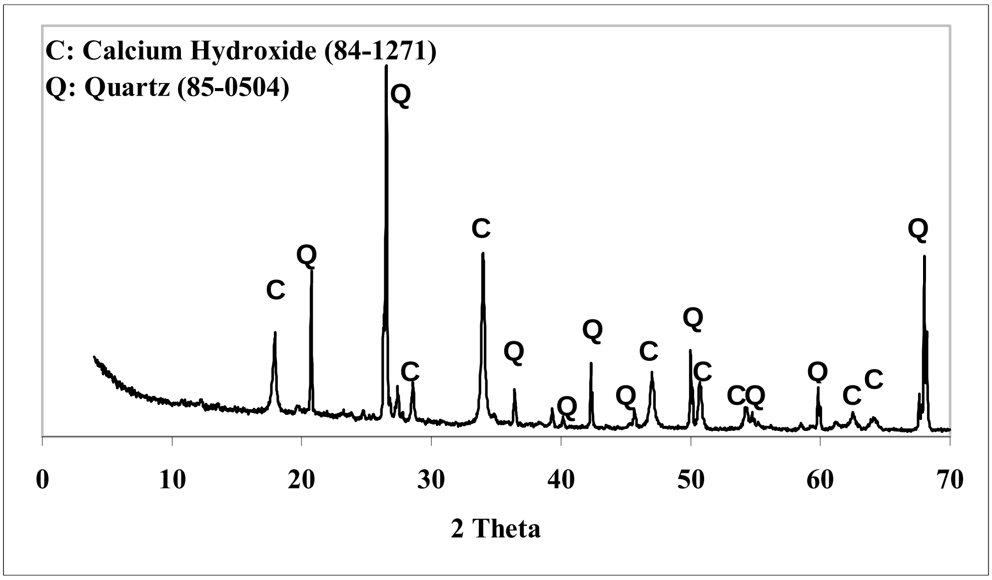


Figure 4.51. XRD analysis result of sample K244 (25 °C), B/Ag Ratio 1:3 (3 months of carbonation)

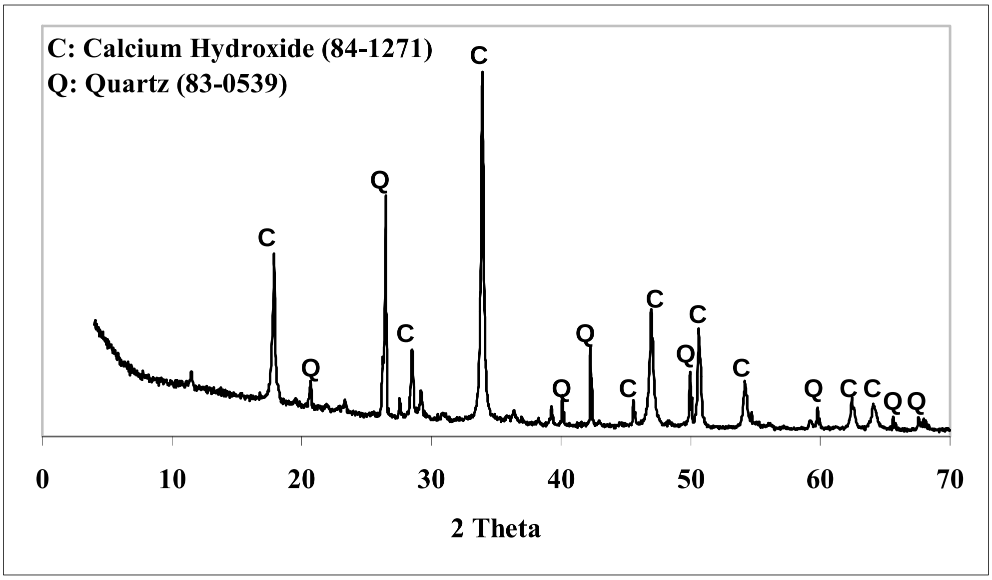


Figure 4.52. XRD analysis result of sample K-244(600°C), B/Ag ratio 1:3 (3 months of carbonation)

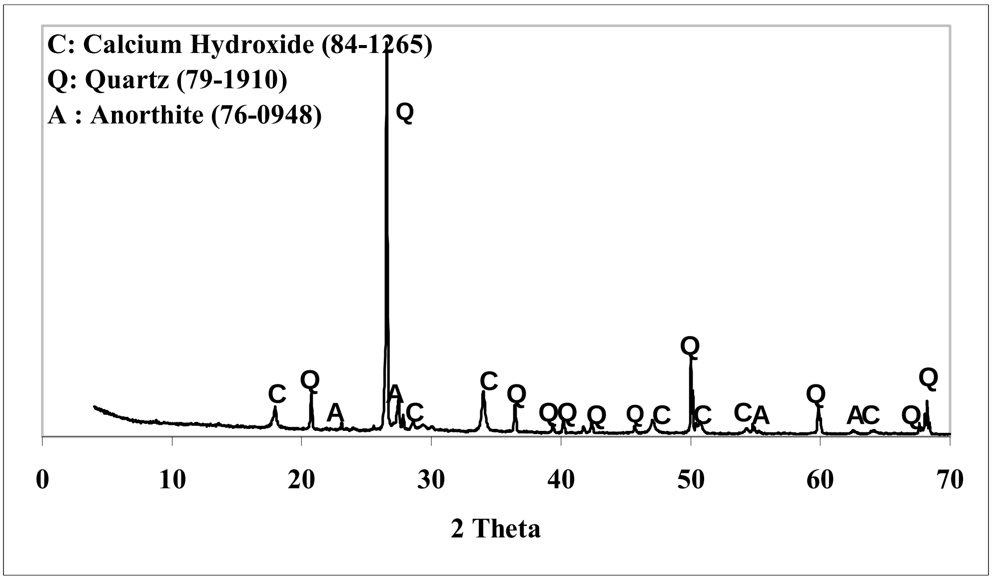


Figure 4.53. XRD analysis result of sample K-244 (1000 °C) B/Ag ratio 1:3 (3 months of carbonation)

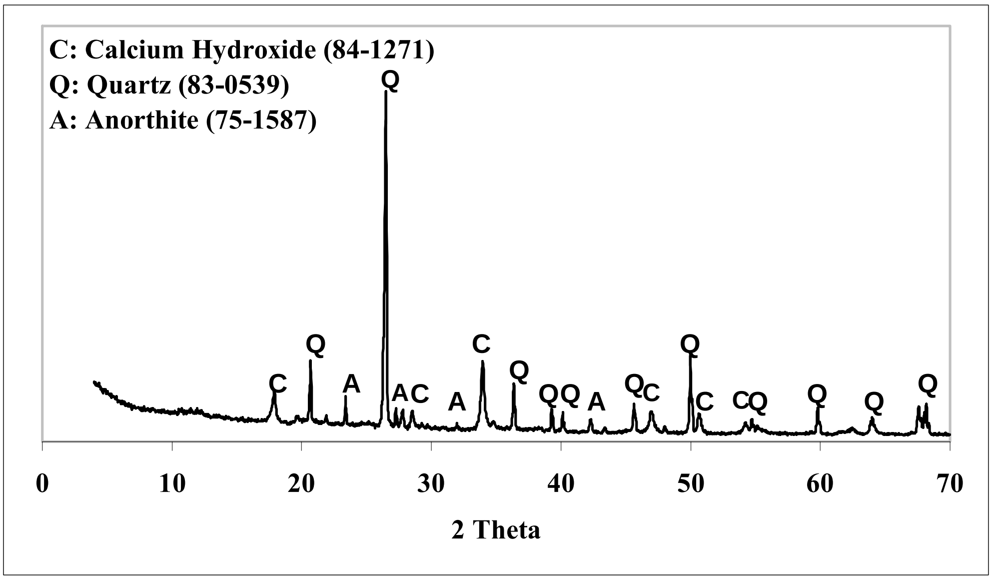


Figure 4.54. XRD analysis results of sample K-103 (NP), B/Ag ratio 1:6 (3 months of carbonation)

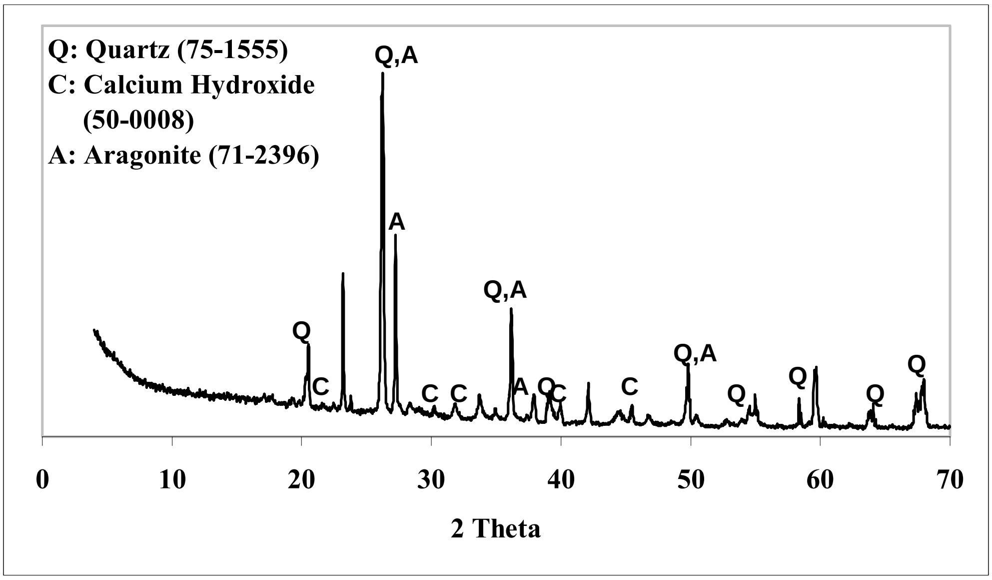


Figure 4.55. XRD analysis result of sample K-244 (600°C), B/Ag ratio 1:6 (3 months of carbonation)

Regarding to the results, the three months of carbonation time is too short for making a healthy decision about the suitable type of pozzolana and binder aggregate ratio that should be used in preparation of intervention mortar.

The second part of tests has been applied after 5 months of carbonation. The XRD analysis test results of samples after 5 months of carbonation are given in Figure 4.56-Figure 4.63.

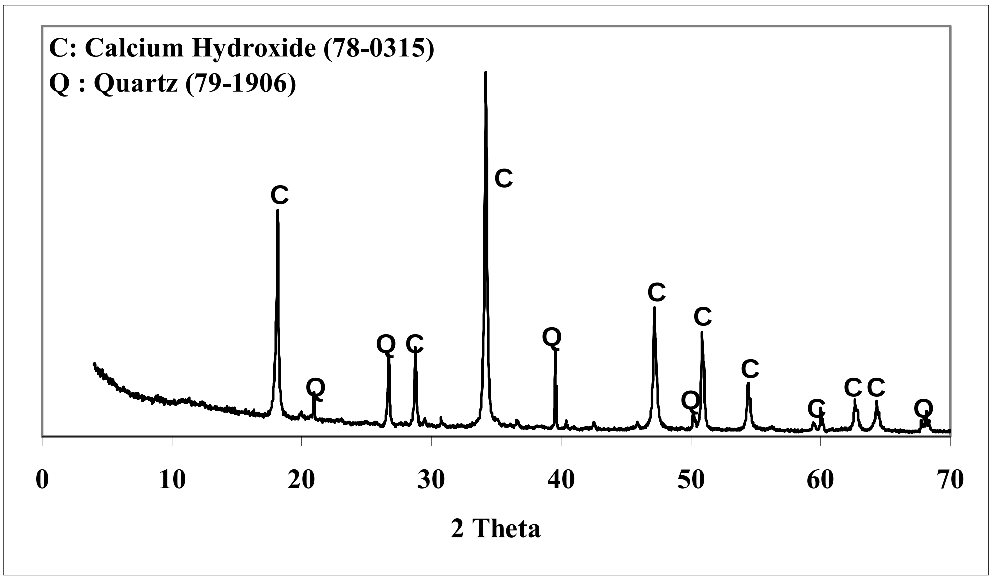


Figure 4.56. XRD analysis result of sample K-103 (NP), B/Ag Ratio 1:1 (5 months of carbonation)

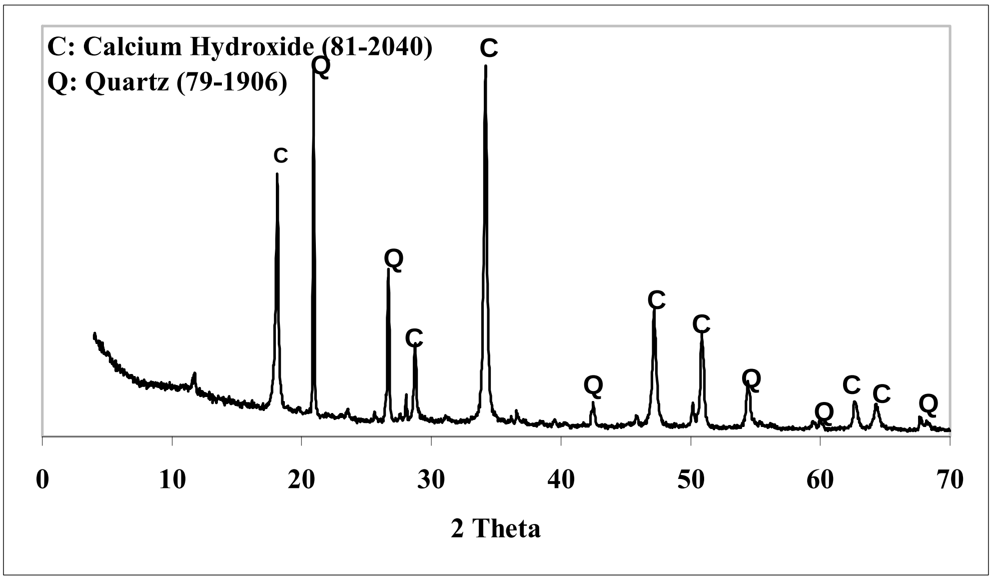


Figure 4.57. XRD analysis result of sample K244 (600 ^{o}C) B/Ag Ratio 1:1 (5 months of carbonation)

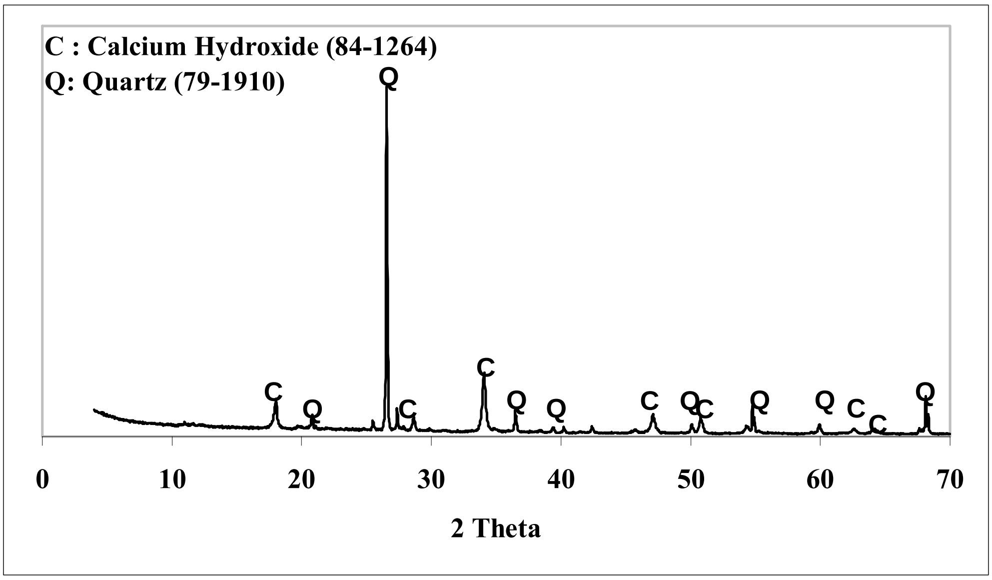


Figure 4.58. XRD analysis result of sample K-103 (NP), B/Ag ratio 1:3 (5 months of carbonation)

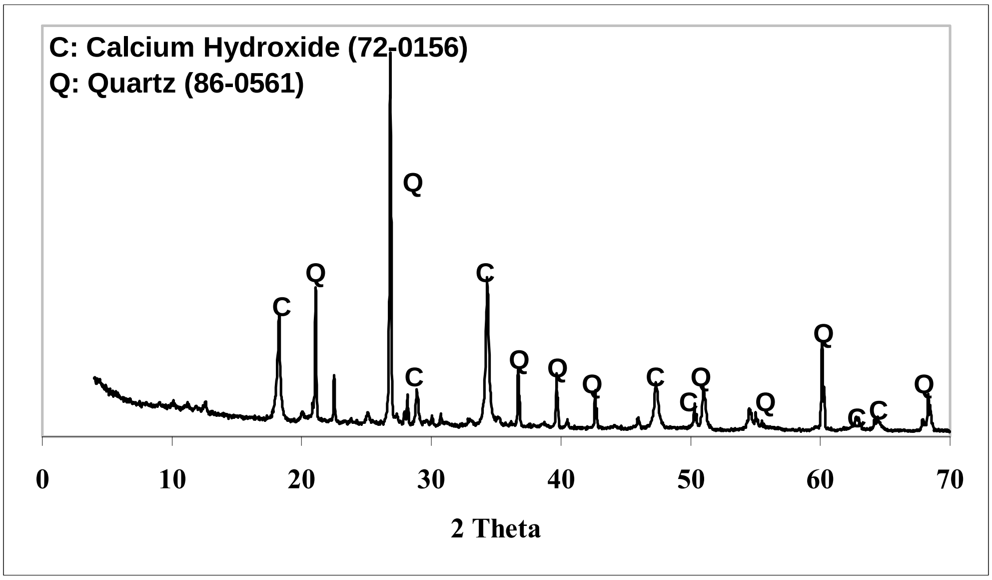


Figure 4.59. XRD analysis result of sample K-244 (25 ^{o}C), B/Ag Ratio 1:3 (5 months of carbonation)

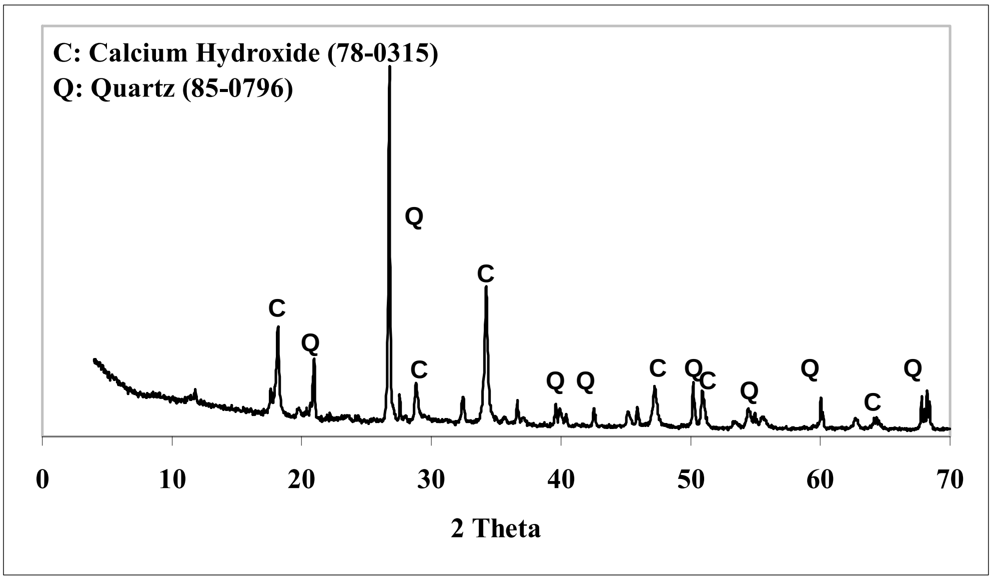


Figure 4.60. XRD analysis result of sample K-244(600°C), B/Ag ratio 1:3 (5 months of carbonation)

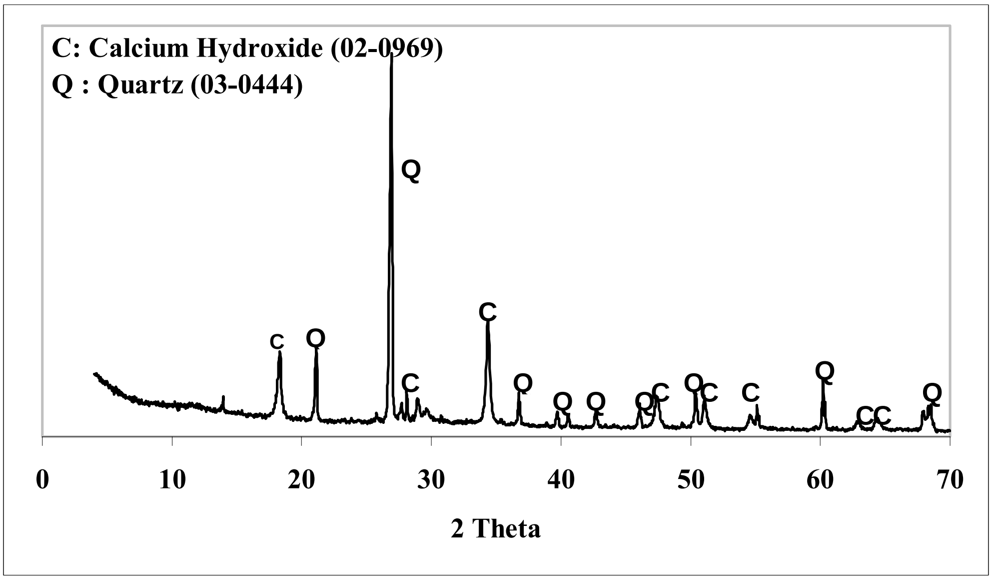


Figure 4.61. XRD analysis result of sample K-244 (1000 °C) B/Ag ratio 1:3 (5 months of carbonation)

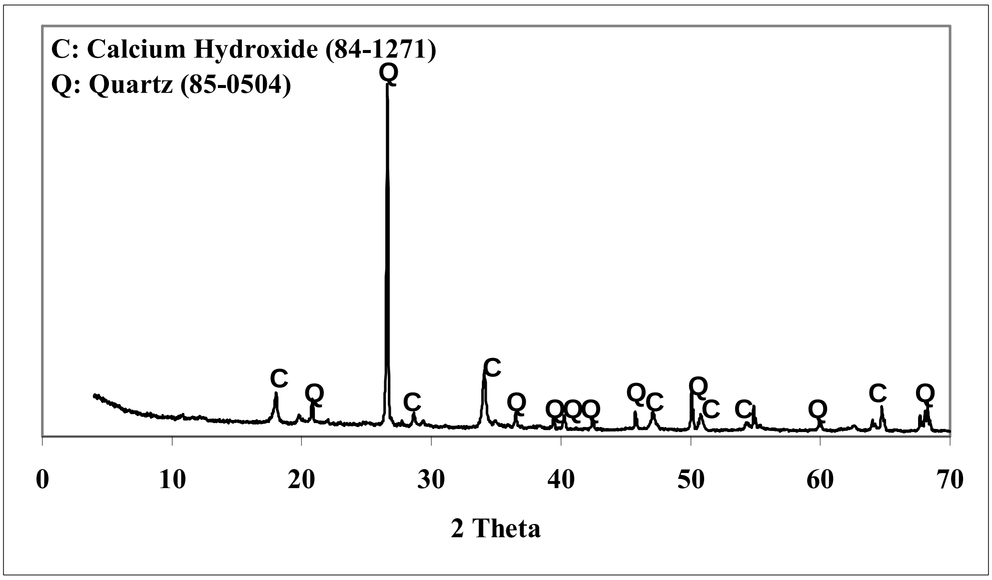


Figure 4.62. XRD analysis results of sample K-103 (NP), B/Ag ratio 1:6 (5 months of carbonation)

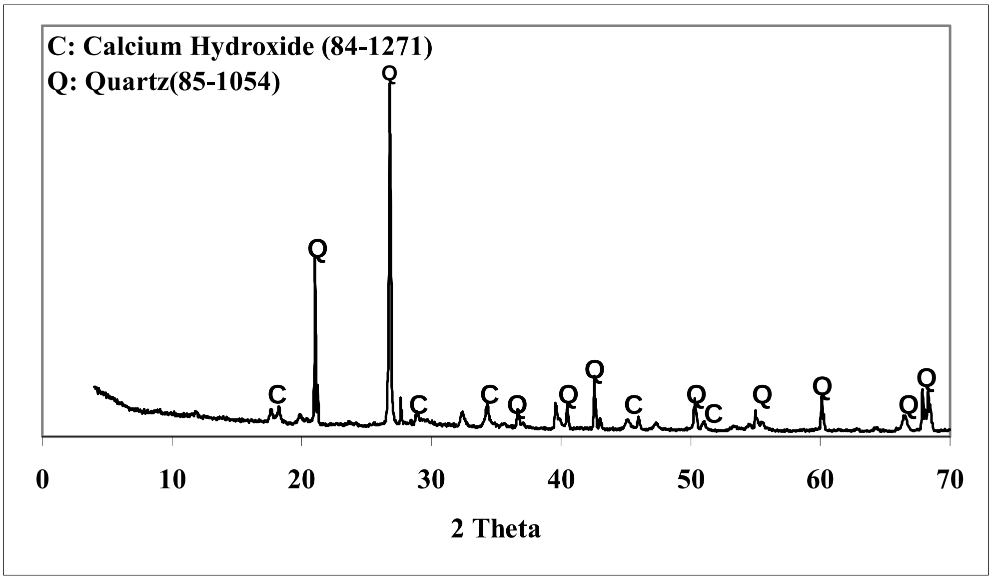


Figure 4.63. XRD analysis result of sample K-244 (600°C), B/Ag ratio 1:6 (5 months of carbonation)

The five months of carbonation time is still not enough for making a healthy decision about the suitable type of pozzolana and binder aggregate ratio that should be used in preparation of intervention mortar

The binder/aggregate ratio, water/binder ratio, and the types of pozzolana used in preparation of mortar samples and the compressive test results (3 and 5 months of carbonation) are given in Table 4.9. According to these results, it can be said that the samples prepared by K-244 (600°C) gained higher compressive strength value than the other samples, but the decrease of compressive strength value after 2 months than the first tests (3 months of carbonation) is an unexpected result. The sample K-103 (NP) did not produce good strength values at all levels of B/Ag ratios.

The binder aggregate ratio has important effect on mechanical property of mortar. Low amount of aggregate can cause internal and surface cracks due to binder increment. Lime fraction abandons its binder function and acts as filler. Therefore, certain amount of aggregate must be present in the mortar (Lanas et.al. 2003). According to the results of compressive strength tests the best combination of B/Ag ratio and type of pozzolana, which can be used for production of intervention mortar, is 1 part of lime and 3 parts of aggregate with pozzolana (K-244) which is heat treated at 600°C. The 5 months of carbonation time was too short to distinguish samples. The results obtained from the 3 and 5 months of carbonation are preliminary results. For making a healthy decision, the samples should be carbonated 1 year at least.

Table 4.9. B/Ag ratio, W/B ratio, Types of Pozzolanas used in preparation of mortar samples and the Compressive Strength Test results (3 and 5 months of carbonation) of mortar samples

B/Ag	Pozzolana Types	Water/Binder Ratio	Compressive Strengths of the Three Samples (MPa) (3 Months)			Average	Compressive Strengths of the Three Samples (MPa) (5 Months)			Average
1/1.	K-103 (NP)	0.82	1.08	0.77	-	0.93	0.99	0.96	0.86	0.94
1/1.	K244(600°C)	0.91	1.08	1.05	1.71	1.28	1.41	1.89	2.32	1.87
1/3.	K-103 (NP)	1.21	1.33	0.39	0.84	0.85	0.98	0.88	0.88	0.91
1/3.	K244(25°C)	0.99	0.82	0.78	-	0.8	1.01	0.92	-	0.97
1/3.	K244(600°C)	1.01	4.46	4.94	5.75	5.05	2.59	3.07	3.3	2.99
1/3.	K244(1000°C)	1.03	1.84	2.43	-	2.14	2.65	2.96	2.63	2.75
1/6.	K-103 (NP)	1.89	0.98	0.76	1.05	0.93	1	1.53	1.17	1.23
1/6.	K-244(600°C)	1.52	3.24	3.28	3.38	3.3	3.15	2.48	2.71	2.78

CHAPTER 5

CONCLUSIONS

The mortar and brick samples collected from Manisa Çukur Hamam (Turkish Bath) and Hacet Mescidi (Mosque) were characterized and potential intervention mortars for these two structures were produced according to characteristics of mortar samples.

Lime mortars used in the stone and brick walls of the two buildings had similar appearance and texture. The binder/aggregate ratios of mortars were between 1:4-1:2 by weight. The mortars were composed mainly of calcite and quartz. Calcite was derived from the carbonated lime and the quartz from aggregates.

The particle size distributions of aggregates were similar. Aggregates greater than 1180 μm composed the largest fraction of the aggregates. The fine sized fractions of the aggregates were found to be pozzolanic (<53 μm) and containing high amounts of silica and alumina.

Lime mortars were in compact appearance and the aggregates were firmly embedded in mortar matrix. TGA analysis revealed that all mortar samples were hydraulic.

The results of characterization tests, applied to samples collected from the two structures were used in production of possible intervention mortars.

Binder/aggregate ratios of 1:6-1:1 were studied for potential intervention mortars. Commercial lime was used as binder and standard sand was used as aggregate for the production of intervention mortars. The commercial clay, which was heat-treated at temperatures 25-600-1000^{o}C, was used as pozzolanic source. Samples were prepared by standard procedure and cast in cylindrical molds and allowed for carbonation in a humid environment. The samples that were carbonated for 3 months and 5 months, were tested by XRD and compressive strength tests. Samples with 1:3 binder/aggregate ratios made by mixing heat treated (600^{o}C) commercial clay, provided the maximum strength.

This study provided important data source for material characteristics of the Manisa Çukur Hamam and Hacet Mescidi. The intervention mortars produced in laboratory can not be directly used in restoration of these two structures, because the carbonation time is too short for making a healthy decision about these mortar samples. Therefore, future studies should be carried on using longer carbonation periods by the same procedure. Compressive strength tests performed on mortar samples that were 5 months old showed that modest improvements were obtained from samples that contained heat-treated K-244 clay.

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