ARCHAEOMETRICAL INVESTIGATION OF SOME SELJUK PLASTERS

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Approval of the Graduate School of Natural and Applied Sciences

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

ARCHAEOMETRICAL INVESTIGATION OF SOME SELJUK PLASTERS

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The aim of the study was to investigate Seljuk Plasters used in some of their royal administrative or residential buildings from a viewpoint of their raw materials and technological characteristics. Some Byzantine Plasters of the same period were also investigated to make comparison. Plasters from some historic structures in the archaeological sites namely; Alanya Castle, Kubadabad Palaces, Syedra Archaeological Site, Aspendos Amphitheatre, Selinus Archaeological Site-Şekerhane Köşk and Hasbahçe were examined.

In a series of examination basic physical properties of the plasters as bulk density, porosity, water absorption capacity and water vapour permeability were obtained. The results indicated that plasters are low dense and high porous materials and having good breathing property.

Mechanical properties of the plasters were expressed by the modulus of elasticity (E_{mod}) values which were obtained from ultrasonic pulse velocity measurements. The E_{mod} of the plasters being in the range of 1.0 to 5.6 Gpa show that they have enough mechanical strength comparable to historic mortars and bricks.

Raw material composition and mineralogical properties of plasters were determined by combined interpretation of several types of analyses such as chemical analyses, particle size distribution of aggregates, petrographic analyses of thin sections by optical microscopy, scanning electron microscopic analyses of cross sections coupled with EDX for image analyses and semi-quantitative elemental analyses, X-ray powder diffraction analyses for the determination of mineral phases, thermogravimetric analyses and FTIR analyses. Binder used in all plasters was found to be lime with amount in the range of 53.8-96.8% as $CaCO_3$. The main minerals of aggregates are quartz, calcite (limestone), dolomite and opal-A. Regarding particle size distribution of aggregates it was possible to classify them into fine, coarse and mixed aggregates having rather high pozzolanicity.

Study on decorative and red zigzag patterned plasters indicated presence of haematite as the source of red pigment. Study on green colored plaster also indicated presence of iron containing mineral with lower oxidation state.

The Seljuk and Byzantine Masonries chosen are still surviving buildings that their plasters should be of good quality. In fact, this study approved their quality which may be due to the presence of opal-A and dolomite.

Keywords: lime plaster, Anatolian Seljuk Period, Byzantine Period, haematite, opal-A, pozzolanicity

ÖZ

BAZI SELÇUKLU DÖNEMİ SIVALARININ ARKEOMETRİK YÖNDEN İNCELENMESİ

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Bu çalışmanın amacı, Selçuklu Dönemi idari ve sivil yapılarının bazılarındaki sıvaları hammadde özellikleri ve teknolojileri yönünden incelemektir. Karşılaştırma yapmak için aynı dönemin bazı Bizans yapılarındaki sıvalar da incelenmiştir. Çalışmada Alanya Kalesi'nden, Kubadabad Sarayları'ndan, Syedra arkeolojik alanındaki bazı yapılardan, Aspendos Anfitiyatrosundan, Selinus arkeolojik alanındaki Şekerhane Köşk ve Alanya'da bulunan Hasbahçe'deki bazı tarihi yapılardan alınan sıva örnekleri incelenmiştir.

Bir grup çalışmada yoğunluk, porozite, su tutma kapasitesi ve su buharı geçirimliliği cinsinden temel fiziksel özellikler belirlenmiştir. Sonuçlar sıvaların düşük yoğunluklu ve porozitesi yüksek malzemeler olduğunu ve su buharına yeterince geçirimli olduklarını göstermiştir. Mekanik özellikler ultrasonik hız ölçümleri ile elde edilen elastiklik modülünün hesaplanması ile belirlenmiştir. Elastiklik modülü 1.0-5.6 GPa olarak bulunmuş ve sıvaların tarihi harç ve tuğlalara yakın mekanik özelliklere sahip olduğu anlaşılmıştır. Sıvaların hammadde bileşimleri ve minerolojik özellikleri, çeşitli analizlerin sonuçları birleştirilerek, belirlenmiştir. Bu analizler; kimyasal analizler, agregaların tanecik boyutu dağılımı, hazırlanan ince kesitlerin optik mikroskopla petrografik analizi, hazırlanan uygun kesitlerin tarama elektron mikroskobuyla incelenmesi ve belirlenen bölgelerde enerji dağılım analizörü ile element miktarlarının bulunması, mineral fazlarının x-ışınları toz difraksiyon ile analizi, FTIR ve termogravimetrik analizlerdir.

Sıvalarda bağlayıcı olarak kireç kullanıldığı ve $CaCO_3$ olarak miktarının 53.8-96.8% olduğu belirlenmiştir. Sıvanın agrega kısmında belirlenen temel mineraller kuvars, kalsit (kireç taşı), dolomit ve opal-A'dır. Agregalar tane boyutu dağılımı bakımından ince, iri ve karışık agrega olarak üç gruba ayrılmıştır ve pozzolanik aktiviteleri özellikle ince agregalarda çok yüksek bulunmuştur. Kırmızı zigzag motifli sıvalarda renk veren madde hematit olarak belirlenmiştir. Yeşil boyalı sıvada ise rengin düşük değerlikli demir içeren celadonit mineralinden ileri geldiği anlaşılmıştır.

Çalışılan Selçuk ve Bizans yapılarının sıvaları ile birlikte günümüze ulaşması, sıvalarının iyi kalitede olduğunu göstermektedir. Bu çalışma da bu durumu destekler nitelikte sonuç vermiştir. Bu dayanıklılıkta esas etmenlerden ikisinin opal-A ve dolomit olduğu düşünülebilir.

Anahtar Kelimeler: kireç sıva, Anadolu Selçuklu Dönemi, Bizans Dönemi, hematit, opal-A, pozolanik özellik.

To My Family

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INTRODUCTION

A monument is not only a document of historical materials but also a witness of historical techniques and technologies. Due to the absence of documentation on those technological information, it is obvious that the standing monuments and their material substances are the only sources at hand to be explored. In this context, conservation studies have to secure the historic building materials as well as the information they include on production and construction technologies. Therefore, the most important aim of conservation is to preserve the material state of a monument in which it has come down to present and prevent further loss of substance (Sasse and Snethlage, 1996).

In the field of archaeometry, the investigation of historic building materials and their technologies are important subjects to be studied. Those studies are also important for restoration and conservation disciplines especially for the preparation of compatible repair materials as well as for the building science discipline to be informed on the historical context of the materials science. In addition, the knowledge obtained from these studies initiates development in building science.

1.1 The Role and Importance of Plasters in Ancient Masonry

Plaster is undoubtedly the oldest type of finishing material which has been identified in the very old buildings such as those of Neolithic site Çatalhöyük (Cessford, 2001). It serves important functions in the masonry. Depending on their functions, the original plasters of historic buildings store valuable technological information. Therefore, they should be preserved with as little renewal as possible.

The main function of the plaster is to protect the masonry against weathering conditions, such as wetting and drying cycles, freezing and thawing cycles, salt crystallization cycles, due to the changes in ambient temperature, humidity conditions and wind flow. These weathering conditions and atmospheric pollution are the factors affecting the deterioration of all building materials including plasters through some physical, physico-chemical, chemical and microbiological mechanisms (Schaffer, 1972; Malinowski, 1981; Caneva et. al, 1991).

Plaster keeps the masonry underneath healthy and durable against most weathering conditions. It may have several other functions such as the improvement of acoustical and thermal performance as well as the fire resistance of the wall (Callender, 1982). The plasters in ancient masonry are known to affect the water vapour permeability of the walls through their 'breathing property', letting the passage of water vapour through the wall. In addition, plaster improves the appearance of the wall by hiding the imperfections of rough work and gives it an attractive texture compatible with the local environment (Houben and Guillaud, 1994).

Excessive humidity is destructive for the masonry. Humidity may enter the masonry in different ways and forms, such as rain water, fog, rising damp, condensation etc. (Koller,1979). Excess humidity in the wall should come out of the wall as quickly as possible, otherwise, it may cause several decay problems (Akkuzugil, 1997). At that point, plasters have an important role on 'breathing property' of the walls, by letting out the excess humidity (Szczerba and Jedrezejewska, 1988).

Unfortunately, historical buildings suffer badly from large amount of excess water and humidity, after restorations with new plasters of poor water vapour permeability.

The ‘breathing ability’ of the historic masonry specified as water vapour permeability of its materials has to continue after the restoration, as well as its other characteristics. That is why water vapour permeability and other important physical and mechanical properties of the historic plasters, their raw materials characteristics which influence their performance has to be well investigated. By only this way, it may be possible to prepare compatible repair materials like repair plasters (Szczerba and Jedrzejewska, 1988).

1.2 Ancient Plasters

The major components of plasters are the binder and the filler which may also be called as aggregates. Performance of the plaster is directly related with the properties of its components. In other words the components of plaster, such as mud, lime or gypsum as binder, different types of inorganic aggregates as filler, and organic and/or inorganic additives directly influence its performance. Therefore, characteristics of these components and their contributions to the performance should be well evaluated (Wickens, 1984; Martinez-Ramirez et. al 1995; Baronio et. al 1997; Middendorf and Knöfel, 1998 a, b; 1999; Young and Miller, 2000; Tunçoku, 2001; Dheilly et. al, 2002; Seabee et. al, 2003).

Ancient plasters can be classified into three groups with respect to binder; mud, gypsum and lime plasters.

1.2.1 Mud Plasters

This is simplest and most primitive type of plaster. It is based on clay, silt, sand reinforced with chopped straw or other fibrous materials and sometimes with dung. Mud plaster has been used as a surface coating over adobe itself, since it is composed of similar material to adobe, it bonds well to it. Mud plaster itself is not resistant to water. Periodical application of mud plaster may end up with satisfactory results or other coats such as lime, which are more resistant to water may well be used (Davey, 1961; Brown and Clifton 1978).

The mechanical property of mud is very low. In order to increase its strength and to avoid cracking, admixtures such as grass, straw, wheat or rye chaff, animal dung or hair were added. Other known admixtures are tannic acid, jute fiber, cattle urine, sawdust, woodshavings, hardwood ashes etc. (Davey, 1961; Brown and Clifton 1978; French, 1987).

1.2.2 Gypsum Plasters

The earliest gypsum usage was seen in Egypt both as a mortar among blocks of stone in pyramids and as a plaster at the beginning of the third millennium B.C. It was also used in Mesopotamia from very early times (Davey, 1961; Torraca, 1982). Gypsum plasters are more durable than mud plasters.

Gypsum plasters or mortars are prepared by heating gypsum mineral or selenite rock (both are composed of hydrated calcium sulphate), at rather moderate temperatures, either at around 130^0 C or at around $200\text{-}400^0$C to get hemi-hydrate and anhydrite respectively. If the gypsum mineral is heated to high temperatures such as $900\text{-}1300^0$C, a substance ($CaSO_4$. nCaO) called hydraulic or flooring plaster is obtained (Davey 1961).

At moderate heatings, hemihydrate and anhydrite are obtained by the following reactions:

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O\ (s)} \xrightarrow{130^0C\text{””}} \underset{\substack{\text{Plaster of Paris}\\ \text{(hemi-hydrate)}}}{CaSO_4.1/2\ H_2O\ (s)} + 3/2\ H_2O(g)$$

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O\ (s)} \xrightarrow{200\text{-}400^0C} \underset{\text{Anhydrite}}{CaSO_4\ (s)} \quad + \quad 2\ H_2O(g)$$

There are many types of gypsum plasters. Some of them were used in the past and some other types are still being used.

Plaster of Paris sets rapidly when mixed with water, forming hard crystalline gypsum. Varying sorts of retarders such as keratin or glue-like materials were added to prevent rapid setting (Davey, 1961). In case of anhydrite, since it hardens rather slowly, some accelerators were needed to be added such as alum, borax or soda and various patented brands were produced (Davey, 1961). Although gypsum is quite soluble in water, it was used even in underground parts of many medieval buildings with hydraulic lime and/or other additives (Middendorf and Knöfel, 1994). In many aspects, historic gypsum technologies are worth studying.

1.2.3 Lime Plasters

Lime plasters are being used from the ancient times, even in Neolithic period, until the beginning of 20th century, all over the world. Lime is an essential component of lime mortars and plasters. It is an artificial product, made by heating limestone or sea shells in large kilns. Marble is not suitable source of calcium carbonate, because its large grains form lumps of quicklime that are not easily slaked (Torraca,1982).

Lime plasters will be discussed in more detail for the properties of the binder lime, the filler (aggregates), and additives.

1.3 Properties of Binder Lime

The properties of binder lime will be discussed in several aspects under the titles of “raw materials and the types of lime” and “carbonation of lime”.

Raw Materials and the Types of Lime: Limestone, being the source of lime, is formed of mineral calcite, which is calcium carbonate ($CaCO_3$), chemically composed of 56% calcium oxide and 44% carbon dioxide (CO_2). Such a pure form of calcite however, is hardly found in the nature. During or after the formation of rock, a certain amount of magnesia (MgO) and other impurities such as silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3), and alkalies such as sodium and potassium oxides in the form of complex silicates are always introduced. The quantity of these impurities determines the type of limestone and the resultant lime respectively (Eckel,1928; Davey,1961; Boynton,1966). When limestone is heated in kilns at the temperatures around 900^0 C, carbon dioxide is given off .The calcium oxide (CaO) produced is called quicklime or unslaked lime.

$$CaCO_3(s) \xrightarrow{900^0C} \underset{\text{quicklime}}{CaO(s)} + CO_2(g)$$

Quicklime is slaked by treating the powdered or lump quick lime with water. Slaked lime is also called lime hydrate or lime putty.

$$CaO\ (s) + H_2O\ (l) \longrightarrow \underset{\text{Slaked lime}}{Ca(OH)_2\ (s)} + \Delta H \qquad \Delta H = -8.68\ \text{kcal/mol}$$

Pure slaked lime in crystalline form is called portlandite. Portlandite is a hexagonal crystal with a specific gravity 2.24 g/cm^3. Some properties of slaked limes are given in Table 1.1.

Table 1.1 Properties of slaked limes (Canonge et al,2001)

Type	Solubility (g/100g soln)	Surface area (cm^2/g)	Bulk density (g/cm^3)	Specific gravity
Fat lime	0.165(20^0C)	8000-20000	0.49-0.7	2.20-2.50
Hydraulic lime	Same	3000-8000	0.7-1.0	2.60-2.90

Types of slaked lime are fat lime or hydraulic lime depending on the amount of impurities in it (Table 1.1). If the amount of impurities, expressed as the oxides of magnesium, silicon, aluminum and iron, is less than 5%, the lime is named as fat lime, rich lime or high calcium lime. If the impurities exceed 5%, the lime is no more high calcium lime. It gains hydraulic properties i.e., setting without the need of carbon dioxide in the air, due to the oxides of silicon, aluminum and iron in its composition. Hydraulic limes can be further classified into several sub groups depending on the amount of impurities in it and its cementation index (Boynton, 1966; Holmes and Wingate, 1997). Cementation index is defined by the following equation:

$$\text{Cementation Index (CI)} = \frac{2.8(\%\text{SiO}_2) + 1.1(\%\text{Al}_2\text{O}_3) + (\%\text{Fe}_2\text{O}_3)}{\%\text{CaO} + 1.4(\%\text{MgO})}$$

The values given in the equation correspond to percent composition of acid soluble part of hydraulic lime. Some C.I values of hydraulic limes are given in Table. 1.2.

Table 1.2 Cementation Index for Various Types of Limes (Holmes and Wingate, 1997)

Lime Description	Cementation Index	Active Siliceous Compounds
Fat Limes	Close to Zero	Very Little
Slightly (or weakly) Hydraulic Limes	0.3 to 0.5	Around 8%
Moderately Hydraulic Limes	0.5 to 0.7	Around 15%
Eminently Hydraulic Limes	0.7 to 1.1	Around 25%
Natural Cements	1.7	Up to 45%

Carbonation of Lime: Slaked lime is transformed to calcium carbonate by the help of atmospheric CO_2 and water to perform as binder in plasters and mortars. The carbonation occurs by the following reaction;

$$Ca(OH)_2\ (s) + H_2CO_3(l) \rightarrow CaCO_3\ (s) + 2H_2O\ (l \text{ or } g) + 74kJ$$

The environmental conditions which influence this reaction are relative humidity, temperature and atmospheric CO_2 (Dheilly et al, 2002). Relative humidity directly influences the reaction. On the other hand, it is well known fact that solubility of CO_2 decreases as temperature increases.

In humid atmosphere the reaction occurs in the following three sequential steps; a) physical adsorption of water at the $Ca(OH)_2$ grains' surface, b) The dissolution of $Ca(OH)_2$ into Ca^{2+} and OH^- ions, in addition, the dissolution of CO_2 under the basic pH (pH> 10), yielding CO_3^{2-}ions. c) the precipitation of $CaCO_3$. The progress of the reaction gets difficult due to CO_2 diffusion through $CaCO_3$ which has low porosity. However, in an atmosphere with low level of CO_2, low temperatures such as 10^0C, high relative humidity such as 100% conditions lead to complete carbonation of powder $Ca(OH)_2$ within 25 days

(Dheilly et al, 2002). If a lime paste with water/$Ca(OH)_2$ mass ratio of one is used in an atmosphere with low level of CO_2, reaction is not complete even after 30 days since the calcium carbonate film that forms on the surface, interferes with the CO_2 diffusion. This is not the case with the humid powdery hydroxide.

In all types of lime plasters, lime acts as binder and there is an aggregate part, which is generally sand. But, some lime plasters may not contain appreciable amounts of aggregate part. In that, some admixtures of reinforcement such as animal hair or very thin straw may be added.

1.4 Properties of Aggregates

Aggregates are the fillers of natural or artificial in origin, that function as a rigid skeleton for lime-based grounds (Mora et al.,1984). Lime itself, although a good binder., does not have enough strength, contracts on drying and develops cracks. it needs aggregates and/or some admixtures to build up an internal framework.

Some aggregates are inert and don't react with lime. Some others react with the lime in variable degrees. The common aggregates are sands of river or coastal beds.

Pozzolanic aggregates are defined as fillers or additives, though not cementitious in themselves, contain the compounds such as silica, alumina and iron oxides, which readily react with lime at ordinary temperatures in the presence of water, and form stable insoluble compounds with cementing properties (Ashurst and Dimes, 1990; Tunçoku, 2001). Such materials may be of natural or artificial origin.

Natural pozzolanic aggregates are usually of volcanic origin, such as volcanic dust and ash. They may also be of biogenic and /or chemical origin such as diatomaceous earths, siliceous rocks of biogenic origin (petrified wood and plant remains) and silica of organic origin such as; cherts, flints, shales, sandstones and opal (Lea, 1970; Diamond, 1976; Drees et al., 1995; Tunçoku, 2001).

Artificial pozzolanic aggregates are produced by heating materials rich in clays within a temperature range of 600-900^0 C (Baronio and Binda 1997). The treatment causes, through the loss of combined water, the collapse of the crystallographic structure of the clay and the formation of silica and alumina in an amorphous state or in a state characterized by disorder in the lattice structure. In these conditions, silica and alumina undergo pozzolanic reactions with $Ca(OH)_2$. If the thermal treatment overcomes 900°C, alumina and silica can be reorganized again into new thermodynamically stable compounds (mullite, tridimite, etc.) with no reaction properties with $Ca(OH)_2$ (Baronio and Binda, 1997).

Opal is the most reactive pozzolanic constituent It may be present mainly as crystalline form opal-CT and X-ray amorphous form of opal-A, which is hydrous silica ($SiO_2.nH_2O$) (Drees et al., 1995; Tunçoku, 2001).

Pozzolanic effect can arise by the reaction between lime and pozzolanic material which can be summarized as follow (Torracca, 1988).

$$\underset{\substack{\text{Slaked}\\\text{Lime}}}{\text{CH}} \quad + \quad \underset{\substack{\text{Pozzolanic}\\\text{material}}}{\text{S}} \quad + \quad \underset{\text{water}}{\text{H}} \quad \longrightarrow \quad \underset{\substack{\text{Calcium Silicate}\\\text{Hydrate}}}{\text{CSH}}$$

The calcium silicate hydrate forms a network of fibrous crystals or gelatinous amorphous material which may be considered as the main cause of increasing durability in plaster or mortar.

The grain size distribution and the average grain size of the aggregates in a given plaster or mortar is effective on its physical and mechanical properties. Excessive use of fine sand, for instance, will provide higher surface area to be covered with binder, which means more water and which results in a porous plaster or mortar with lower strength (Ashurst and Dimes, 1990; Schafer and Hilsdorf, 1993). Another important property of aggregate particles is their shapes which are also effective on the physical and mechanical properties and the workability of plaster or mortar. It is suggested that aggregates with rough surfaces provide larger specific area. In spite of difficulties in the workability with such a plaster or mortar, the aggregate of this kind provides higher strength and better adherence with the binder (Mora et al., 1984; Tunçoku, 2001).

1.5 Additives

Historic plasters and mortars may have some inorganic and organic additives besides the binder and the aggregates. The inorganic additives such as sepiolite ($2MgO.3SiO_2. 4H_2O$), or metakaolin which is prepared by heating kaolinite at around 600-850^{0}C, or Opal-A ($SiO_2.nH_2O$) are thought to affect the carbonation reaction in the positive way (Martinez-Ramirez et. al. 1995; Tuncoku, 2001; Güney, 2003). Organic additives such as eggwhite, blood, rye dough, fig juice, hog’s lard, casein, fats, curdled milk, oils, animal hairs etc. were probably used to improve workability, to extend or retard the setting time, to increase cohesion and the strength of plasters and mortars (Sickels, 1981; Knöfel and Wisser, 1988). Some experimental work showed that oleates influence the crystallization of calcium carbonate in a positive way (Young and Miller, 2000). Oleates are known to be abundant in olive oil. Such organic additives, if added, will affect carbonation as well as the final properties of calcium carbonate even at very low concentrations.

1.6 Pigments

Some of the historic building plasters were decorated with wall paintings. Pigments used in wall paintings may be classified into various categories such as; mineral pigments of natural or artificial origin, organic pigments of animal or vegetable origin, and synthetic pigments (Mora et al., 1984).

Natural mineral pigments are present in the form of oxides, sulphides, carbonates, sulphates etc. Artificial mineral pigments are usually chemical products of well defined composition which were obtained by dry method, like cinnabar being produced by sublimation, or by wet method through precipitation of chemical solutions.

The most common red pigment in some Roman wall paintings was haematite which was present in three forms such as well crystallized, poorly crystallized and disordered haematite (Bearat, and Pradell, 1997). Well crystallized haematite was most common, described in ancient Roman texts by Pliny used for the sinopis, may be originating from Sinop. It was almost pure pigment but had different hues: blood red, ochre, deep brown and violet. The poorly crystallized haematite was associated with quartz, plagioclase, potassium feldspar, illite and kaolinite being the typical composition of red ochre (Bearat and Pradell, 1997). Bearat and Pradell thought that this type of haematite constitutes a lower quality pigment corresponding most probably to the *Rubrica* described by Pliny (Bearat and Pradell, 1997). The disordered haematite could be obtained by dehydration of goethite (yellow ochre) by heating it at temperatures lower than 850-900^0 C, above this temperature, well crystallized haematite is produced. Its tint varies from orange to deep brown depending on the heating temperature (Bearat and Pradell, 1997). However its origin, whether natural or artificial, is under discussion by several researchers (Bearat and Pradell, 1997)

The predominant green pigments in Roman wall paintings are green earths and particularly celadonite. They were sometimes applying their green earth pigment over a yellow ochre undercoat to improve the adherence of the green paint to the lime plaster (Bearat and Pradell, 1997).

The white pigment is usually calcite of natural origin but it might be artificially prepared as described by Cennini in 15th century Florence (Cennini, 1960). According to Cennini, air-slaked lime is put into powder and mixed with clear water everyday, for eight days, then made to a cake , left in the sun as long as possible , powdered and made to the cake again, left in the sun, grinded thoroughly and used by mixing it with water on wet lime plaster of fresco (Cennini, 1960).

Natural organic pigments were obtained from substances contained in some parts of animals, from decoction or maceration of wood, fruits, leaves, bark or roots of plants. Synthetic organic coloring substances may be of dye stuffs, derivatives of aniline, phenols, quinones etc. (Mora et al., 1984).

1.7 Aim of the Study

Byzantine and Seljuk cultures are two overlapping cultures that have affected a large part of Anatolia, especially in medieval period. In spite of many studies on these two cultures such as the architectural and stylistic features of their buildings, the technological characteristics of their building materials such as plasters attracted little attention (Güleç, 1992; Akkuzugil, 1997; Akyazı, 1998; Nizamoğlu, 1998).

The aim of this study is to investigate some Byzantine and Seljuk plasters used in some of their royal administrative or residential buildings from a viewpoint of their raw materials and technological characteristics. The information on those characteristics is thought to be essential for the development of materials to be used for their repair and conservation (Tunçoku et. al, 1993; Sasse and Snethlage, 1996; Middendorf and Knofel, 1998)

The Byzantine and Seljuk masonries chosen are still surviving buildings that is their plasters should be of good quality. In general, the survival of ancient buildings also depends on the use of proper and durable building materials in the past, such as plasters and mortars. Their compatibility with the other materials used in the masonry forming architectural and structural elements must have also contributed to the durability and the survival of those historic structures. A repair material used without primary experiments related with physical and mechanical properties and the performance characteristics of the original materials may cause incompatibility and damage within the original fabric (Sasse and Snethlage, 1996). Therefore, detailed investigation on the properties of historic plasters may give information about a good functioning plaster as well as the specifications and preparation of the repair plasters to be used in restorations of decayed masonry.

In this study, properties of some Byzantine and Seljuk plasters from some historic structures in the archaeological sites namely; Alanya Castle, Kubadabad Palaces, Syedra Archaeological Site, Hasbahçe, Selinus Archaeological Site - Şekerhane Köşk, and Aspendos Amphitheatre were examined.

CHAPTER II

MATERIALS AND METHODS

Analyses of the plasters involved visual characterization of samples coming from six different locations, determination of basic physical and mechanical properties, raw material composition and mineralogical properties of some selected representative samples.

Analyses of basic physical properties were done by the determination of porosity, density, water absorption capacity and water vapour permeability of plaster samples.

Analyses of basic mechanical properties were done by measurement of ultrasonic pulse velocity to determine modulus of elasticity.

Raw material composition and mineralogical properties of selected plaster samples were determined by combined interpretation of several types of analyses such as chemical analyses, particle size distribution of aggregates, petrographic analyses of thin sections by optical microscopy, scanning electron microscopic analyses of cross sections coupled with EDX for image analyses and semi-quantitative elemental analyses, X-ray powder diffraction analyses for the determination of mineral phases, thermogravimetric analyses and FTIR analyses.

Chemical analyses involved the determination of binder and aggregate proportions by acid treatment, the quantitative determination of calcium ion in acid soluble parts with complexometric titration by EDTA, the qualitative spot tests for soluble salts and quantitative determination of soluble salt content by measurement of electrical conductivity and pozzolanic activity estimations in the fine aggregates by the complexometric titration with EDTA.

In addition, some pozzolanic reaction experiments were done with the finest aggregate portions of some plasters in saturated $Ca(OH)_2$ solution.

Finally, preparation of some new plasters were done by using the original aggregates of historic plasters mixed with analytical grade $Ca(OH)_2$. Some plasters were also prepared by using quartz aggregates and analytical grade $Ca(OH)_2$. After 28 days of carbonation, their ultrasonic velocities were measured. The results were used for comparison with historic plasters.

The information on the historic buildings where the plaster samples were taken, descriptions of the plaster samples are given before the description of experimental methods.

2.1 Historic Buildings and Description of the Plaster Samples

Plaster samples of two or three centimeters size were taken from monuments in several archaeological sites including Alanya Castle, Kubadabad Palace, Syedra Archaeological Site, Aspendos Amphitheatre, Selinus Archaeological site and Hasbahçe in Alanya. Some of Alanya Castle samples were collected during the survey of 1970 in Alanya Castle by the Restoration Department of METU. Some others were taken by the supervision of Alanya Museum during this study. Kubadabad Palaces samples were provided by the courtesy of Prof. Dr. Rüçhan Arık during a previous study (Tunçoku, 2001). Those plaster samples on the walls are mostly composed of a fine plaster layer and a finishing layer. Only some have an additional rough plaster layer below the fine plaster layer (Figs. 2.1- 2.6).

2.1.1 Alanya Castle Samples

Alanya Citadel is one of the hundreds of citadels in Anatolia but surviving in rather good condition till now. Its history extends to Hellenistic Period but its magnificent times correspond to Seljuk Period. At the highest altitude of the land, an interior citadel is located which included administrative and military buildings of Seljuks. They are famous for their decorative red zigzag patterned plasters (Redfort, 2001) (Appendix A1).

In the interior citadel, the important buildings are Seljuk Palace built by Alaaddin Keykubad in 1221, a dormitory and a possible depot. Besides, there are two Byzantine Towers decorated with wall paintings, most probably from Byzantine Period. There is also a small Byzantine Church at the center of the interior citadel. The other important buildings in the citadel are two water wells of Seljuk Period which are still in working condition.

The samples from Alanya Castle are described below:

Code : ALP1
Period : Seljuk
Place : Alanya Castle Palace, sultan gate of palace
Type : Interior lime plaster
Visual Features : fine plaster layer with a thickness of 0.73 cm, looks yellow-white (Fig. 2.1a)
Code : ALP2
Period : Seljuk
Place : Alanya Castle Palace, a room of palace
Type : Interior lime plaster
Visual Features : red and white zigzag patterned fine plaster layer with a thickness of 1.49 cm (Fig. 2.1b)
Code : ALP3
Period : Seljuk
Place : Alanya Castle
Type : Interior lime plaster

Visual Features : yellow painted fine plaster layer with a thickness of 1.35 cm (Fig. 2.1c)

Code : ALP4

Period : Byzantine

Place : Alanya Castle, Byzantine Tower with frescoes, southern wall of B11 room

Type : Interior lime plaster

Visual Features : red painted fine plaster layer, with a thickness of 0.58 cm (Fig. 2.1d)

Code : ALP5

Period : Seljuk

Place : Alanya Castle Palace

Type : Exterior lime plaster

Visual Features : fine plaster layer, with a thickness of 1.37 cm (Fig. 2.1e)

Code : ALP6

Period : Seljuk

Place : Alanya Castle Palace

Type : Interior lime plaster

Visual Features : fine plaster layer, with a thickness of 1.49 cm (Fig. 2.1f)

Code : ALP7

Period : Byzantine

Place : Byzantine Church, southern wall

Type : Interior lime plaster

Visual Features : red painted fine plaster layer, with a thickness of 1.03 cm (Fig. 2.1g)

Code : ALP8

Period : Seljuk

Place : Alanya Castle Palace

Type : Interior lime plaster

Visual Features : fine plaster layer, with a thickness of 1.47 cm (Fig. 2.1h)

Code : ALP9

Period : Seljuk

Place : Alanya Castle Palace

Type : Interior lime plaster

Visual Features : fine plaster layer, with a thickness of 2.19 cm (Fig. 2.1i)

(a) ALP1 (b) ALP2 (c) ALP3

(d) ALP4 (e) ALP5 (f) ALP6

(g) ALP7 (h) ALP8 (i) ALP9

Fig. 2.1 Cross Sections of Alanya Castle Plaster

2.1.2 Kubadabad Palaces Samples

Kubadabad Palaces were built by I. Alaaddin Keykubat in 1236. Palaces are located in southwestern shores of Beyşehir Lake near Konya. The site was first excavated in 1965 (Arık, 1968). (Appendix. A2, A3) The excavation still continues.

Kubadabad palaces are famous for their decorative glazed ceramic tiles over the masonry.

The samples from Kubadabad Palaces are described below:

Code : KGP1
Period : Seljuk
Place : Kubadabad Great Palace
Type : Interior lime plaster
Visual Features : fine plaster layer with a thickness of 1.33 cm and looks yellowish-white (Fig. 2.2a)
Code : KGP2
Period : Seljuk
Place : Kubadabad Great Palace
Type : Interior lime plaster
Visual Features : fine plaster layer with a thickness of 2.14 cm, looks yellowish-gray (Fig. 2..2b)
Code : KSP3
Period : Seljuk
Place : Kubadabad Small Palace
Type : Interior lime plaster
Visual Features : fine plaster layer with a thickness of 0.57 cm, looks yellowish-white (Fig. 2.2c)
Code : KSP4
Period : Seljuk
Place : Kubadabad Small Palace
Type : Interior lime plaster

Visual Features : fine and rough plaster layer with a thickness of 1.44 cm, looks yellowish white (Fig. 2.2d)

(a) KGP1 (b) KGP2 (c) KSP3

(d) KSP4

Fig. 2.2 Cross Sections of Kubadabad Palace Plasters

2.1.3 Syedra Archaeological Site Samples

Syedra archaeological site is located in Seki village which is about 20 km from Alanya (Appendix 4). The city unearthed by excavation is found to extend from 7th century BC to 13th century AD. There are several buildings at the site. Some of the buildings with frescoes are still surviving in good conditions. Plaster samples were collected from different buildings. The plasters collected are from 4th century AD.

The samples from Syedra Archaeological Site are described below:

Code : SYDP1
Period : Byzantine
Place : Syedra, street with columns, S10 place
Type : Exterior lime plaster
Visual Features: red painted fine and rough plaster layers, with a thickness of 0.58 (Fig. 2.3a)
Code : SYDP2
Period : Byzantine
Place : Syedra, Akropal Şapel
Type : Interior lime plaster
Visual Features: fine plaster layer, with a thickness of 0.96 cm and looks yellowish white (Fig. 2.3b)
Code : SYDP3
Period : Byzantine
Place : Syedra, street with columns, interior of niche.
Type : Exterior lime plaster
Visual Features: fine plaster layer, with a thickness of 1.09 cm and looks yellowish (Fig. 2.3c)
Code : SYDP4
Period : Byzantine
Place : Syedra, akropal şapel, western wall
Type : Interior lime plaster

Visual Features: fine plaster layer with a thickness of 0.95 cm and looks gray (Fig. 2.3d)

Code : SYDP5

Period : Byzantine

Place : Syedra, street with columns, S10 place

Type : Exterior lime plaster

Visual Features: red painted fine and rough plaster layers, with a thickness of 1.07 cm (Fig. 2.3e)

Code : SYDP6

Period : Byzantine

Place : Syedra, 4th century church ,abscise.

Type : Interior lime plaster

Visual Features: white and black painted, fine and rough plaster layers, with a thickness of 0.39 (Fig. 2.3f)

(a) SYDP1 (b) SYDP2 (c) SYDP3

(d) SYDP4 (e) SYDP5 (f) SYDP6

Fig. 2.3 Cross Sections of Syedra Plasters

2.1.4 Aspendos Amphitheatre Samples

Aspendos is located beside the river Köprüçay renown throughout the world for its magnificent ancient amphitheatre.

Aspendos was one of the first cities in the region to strike coinage under its own name (Appendix 5).

At the beginning of the 13th century, Aspendos began to bear the imprint of settlement by the Seljuks, especially during the reign of I. Alaaddin Keykubat, when the theatre was thoroughly restored, embellished in Seljuk style with elegant tiles and red zigzag patterned plasters on the walls, and used as a palace.

The sample from Aspendos Theater is described below:

Code : ASP1

Period : Seljuk

Place : Aspendos Theatre, in Antalya, exterior wall of theatre

Type : Exterior lime plaster

Visual Features: red-white zigzag patterned, fine plaster layer, with a thickness of 0.55 cm (Fig. 2.4a)

(a) ASP1

Fig. 2.4 Cross Section of Aspendos Amphitheatre Plaster

2.1.5 Selinus Archeological Site Samples

Selinus archeological site is located near Gazipaşa, 45 km from Alanya. The history of the city extends between Roman to Medieval Period.

One of the buildings, which is decorated with red zigzag patterned plasters, may belong to Seljuk period (Appendix 6). It may be used as Köşk named Şekerhane Köşkü (Redfort, 2000).

The sample from Selinus Archaeological Site is described below:

Code : ŞKP1

Period : Seljuk

Place : Selinus Archaeological Site in Gazipaşa-Alanya, Byzantine masonry, which is used in Seljuk period as a köşk (Şekerhane Köşk)

Type : Interior lime plaster

Visual Features: red-white zigzag patterned, fine layered plaster with a thickness of 0.47 cm (Fig. 2.5a)

(a) ŞKP1

Fig. 2.5 Cross Section of Selinus-Şekerhane Köşk Plaster

2.1.6 Hasbahçe (Alanya) Samples

Hasbahçe is one of the largest surviving Seljuk gardens sites with its walls enclose an area of approximately 5.1 hectares. It has also the largest number of pavilion remains (Redfort, 2000) (Appendix 7).

Hasbahçe, meaning the royal garden, lies on the down slope, opposite and slightly to the east of the castle rock of Alanya. The steepness of the slope, necessitating terracing, makes for a garden site not as readily cultivable and irrigable as Şekerhane and Sugözü on the plain below. Be that as it may, several factors conspire to make this the choice for the Sultan's garden.

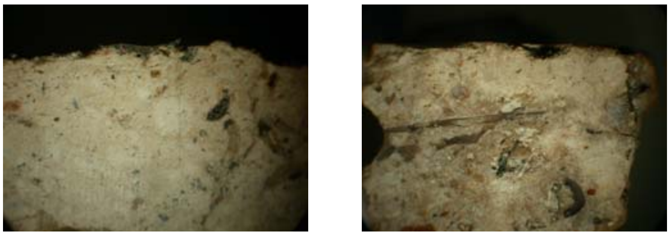
Pavilion H , where the sample HKP1 taken from, is the best preserved of the structure found in this area. The southern and eastern faces of this pavilion are covered with the red zigzag decoration typical of Seljuk buildings.

Pavilion B, where the sample HKP2 was taken from, is located just below the spring. The west and north sides of pavilion B bear traces of the signature, as red and white fresco painted zigzags.

The samples from Hasbahçe Köşk are described below:

Code : HKP1
Period : Seljuk
Place : Hasbahçe Köşk, in Alanya
Type : Exterior lime plaster
Visual Features: red-white zigzag patterned, fine plaster layer, with a thickness of 0.51 cm (Fig. 2.6a)

Code : HKP2
Period : Seljuk
Place : Hasbahçe Köşk, in Alanya
Type : Exterior lime plaster
Visual Features: red-white zigzag patterned, fine plaster layer, with a thickness of 0.77 cm (Fig. 2.6b)



(a) HKP1 (b) HKP2

Fig. 2.6 Cross Sections of Hasbahçe Plasters

2.1.7 Nomenclature of the Samples

In order to simplify the presentation of experimental results, samples are coded. The nomenclature of the samples is given below.

First two or three letters correspond to the building studied. 'P' indicates the plaster. First number corresponds to the sample number. Letters a and b correspond to first fine layer and second rough layers respectively. Small letter 'rp' corresponds to red pigment, 'gp' to green pigment and 'wp' to white pigment of the frescoes of the plasters.

2.2 Determination of Basic Physical Properties

Basic physical properties analyzed are porosity, bulk density, water absorption capacity and water vapour permeability.

2.2.1 Determination of Porosity, Density and Water Absorption Capacity of Samples

Before passing the test procedure, it is better to give related definitions.

Porosity is the empty spaces or voids in a solid mass, expressed as percent volume of the solid mass.

Apparent Volume is the total volume of a sample which includes the pore space.

Real Volume is found by subtracting the pore space accessible to water from the apparent volume.

Bulk (apparent) Density is the ratio of the mass to the apparent volume of the sample.

Real Density is the ratio of the mass to the real volume of the sample.

Water absorption capacity (WAC) is the maximum amount of water which a sample can absorb under the cited conditions, expressed as weight percent of the sample.

The samples are oven dried at around 100^0 C until constant mass and then weighed (M1 g). Then they are placed in a tray and covered with distilled water at room temperature of about 20^0 C and left immersed for 24 hours. They are left under vacuum for about 20 minutes in order to let water enter the pores. Then each sample is taken out of the tray and weighed as immersed in water (M2 g). Then the sample is wiped with a wet paper and weighed again (M3 g). Calculations are carried out by using following equations.

Real Volume = M1 - M2

Real Density = (M1 / (M1 - M2)) x 100

Apparent Volume = M3 - M2

Bulk Density = (M1 / (M3 - M2)) x 100

% Porosity = (1- (Bulk Density/Real Density)) x 100

%WAC= ((M3-M1)/M1)x100

2.2.2 Water Vapour Permeability

For testing the water vapour permeability of the samples, a waterproof cylindrical container for each sample was prepared. A small hole on the side of each container is opened about 1cm below the top of container. The thicknesses of the samples were measured with a vernier. Four measurements were taken and their average value (S_0) was calculated. Then the containers were covered with the samples and sealed at the edges with melted paraffin with the help of a brush. The containers were then filled with water through the side holes and 2cm air space between the sample and the water surface was left. Afterwards, the holes were also sealed with melted paraffin. The relative humidity, atmospheric pressure and the temperature of the room were recorded. The samples were weighed and those weights were recorded as the initial values. The sample sets were weighed periodically until weight loss per unit time became constant.

Calculations were carried out by using the following equation.

$$SD = \mu S_0 = (\psi L * A * (P_1 - P_2) / I) - SL$$

Where;

SD : equivalent air thickness of water vapour permeability, m
μ : water vapour diffusion resistance coefficient, unitless
S_0 : thickness of the sample, m
ψL : constant = $6.89*10^{-6}$ (kg/mh (kg/m^2))
A : test area, m^2
P_1, P_2 : partial vapour pressures on the two sides of the sample, kg/m^2
I : weight change in unit time, kg/h
SL : thickness of air beneath the sample, m

2.3 Determination of Basic Mechanical Properties

Modulus of elasticity was the only mechanical property obtained for the plasters. it was calculated by using ultrasonic velocity measurements of the plasters and their bulk density in an equation.

2.3.1 Determination of Modulus of Elasticity

The modulus of elasticity (E_{mod}) is defined as the ratio of stress to strain and shows the deformation ability of a material under external forces (Timoshenko 1970).

The modulus of elasticity of plasters in this study was determined by ultrasonic pulse velocity measurements (ASTM 2845-90; RILEM 1980). The instrument used was a pulse generating test equipment, PUNDIT plus with its probes, transmitter and receiver of 220 kHz for all samples.

In the method, the impulse is imported to the specimen and the time required for the ultrasonic waves to traverse the minimum cross section of test specimen is measured.

The velocity of the waves is calculated by using the following formula.

$V : l/t$

Where,

V : velocity (m/s)

l : the distance traversed by the wave (mm)

t : travel time (s)

The modulus of elasticity is then obtained through the density of the sample and velocity of wave by the following equation (RILEM,1980).

$E_{mod} = D^{*}V^{2}\ (1+\nu_{dyn})\ (1-2\nu_{dyn})\ (1-\nu_{dyn})$

Where;

E_{mod} : modulus of elasticity (N/m^2)

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

ν : wave velocity (m/sec)

ν_{dyn} : Poisson's ratio

In this equation, Poisson's ratio differs from 0.1 to 0.5. Considering the similarities between plaster, mortar and lightweight concrete, and other case studies for historic mortars investigated, $\nu_{dyn} = 0.18$ seemed to be a reasonable value for this case (Berger 1989; Hidika et al. 1989; Aoki et al. 1989; Topal 1995; Moropoulou et al. 1997, Tunçoku 2001).

2.4 Determination of Raw Material Properties

Raw materials properties of plasters were studied by determination of binder and aggregate proportions, particle size distribution of the aggregates, qualitative and quantitative determination of soluble salts, pozzolanic activity of the fine aggregates, analysis of pozzolanic reaction products on fine aggregates, and by the analyses of mineralogical properties using thin section analysis, XRD, FTIR, TGA and SEM-EDX analyses.

2.4.1.1 Determination of Binder and Aggregate Parts by Dissolution in Acid

The test carried out in this case is the modification of the test procedure given before (Teutonico, 1988).

For the test, the sample was oven dried to constant mass and weighed. Then it was placed in a beaker and 150 ml of 5% HCl solution was added in order to dissolve binder (lime). Solution was left aside until gas evolution was ceased. Then the mixture was filtered through filter paper. Insoluble part was washed until free of chloride ions, dried in oven at about 40^0 C and weighed that corresponded to the aggregate part. By subtracting weight of the aggregate part from dry weight of the sample the weight of acid soluble part was obtained. Results of the experiment were given in Table 2.4.1

2.4.1.2 Determination of Binder and Aggregate Parts by Volumetric Method

This test method was based on the complex formation titration using standard EDTA solution. The solution was prepared by dissolving disodium ethylenediaminetetraacetate salt in distilled water. In the titration 0.01M EDTA solution was used. It was standardized with reference calcium solution prepared from reagent grade pure $Ca(OH)_2$. It is known that EDTA (Y^{4-}) makes one to one stable complex with metal ions.

$$Ca^{2+} + Y^{4-} \rightleftarrows CaY^{2-}$$

Where, Y^{4-} shows anion of EDTA that forms complex with calcium ion.

For this test, 0.200 gr of powdered sample was weighed accurately. Then weighed sample was treated with 3.0 ml of 5% hydrochloric acid in 100 ml volumetric flask. After the dissolution of calcium compounds, volume was made 100 ml with distilled water. Then 20 ml of this solution was taken and diluted to 100 ml, pH of the solution was adjusted to 12-13 using few ml of NaOH 10% and few ml calcon indicator was added. Calcon indicator was prepared by dissolving 0.02 gr calcon indicator in 100 ml ethanol. The final solution obtained was titrated with 0.01M EDTA solution, until a pink color became permanently blue (Black, 1965).

2.4.2 Particle Size Distribution of Aggregates

Classification of aggregates according to the grain size can be made as follows (Norton, 1997).

Size descriptions of gravel, sand, silt and clay according to British and American standards, (BS and ASTM) are given below.

BS

Gravel: 60-2mm

Sand: 2-0.06mm (2000-60μm)
Silt: 0.06-0.002mm (60-2μm)
Clay: <0.002mm (<2μm)
ASTM
Gravel: 100-5mm
Sand:5-0.08mm (5000-80μm)
Silt: 0.08-0.002mm (80-2μm)
Clay: <0.002mm (<2μm)

Size distribution of plaster aggregates was obtained using 1000μm, 500μm, 250μm, 125μm sieves of DIN-4188.

2.4.3.1 Determination of Soluble Salt Content in Plasters by Electrical Conductivity Measurements

The amount of salt in the sample, as percent by weight was determined by measurement of electrical conductivity. For this test, powdered plaster samples were dried in an oven at 40^0C for 24 hours. From each sample 1 g was taken and mixed with 50ml distilled water. The mixtures were left closed for settlement of suspended particles for 24 hours and then filtered. The amount of soluble salt in the samples was determined with the conductivity measurements of the salt extract solutions. Electrical conductivity measurements were done using a conductometer of Metrohm AG Herisau, Kondoktometer E382.

Percent salt in the sample was calculated using the following equations (Black, 1965):

$EC=[(0.0014*R_{std})/(R_{ext})]$ ($mhocm^{-1}$) where;
EC : electrical conductivity
R_{std} : the cell resistance with standard solution (0.01 N KCl)
R_{ext} : the cell resistance with extract solution

% salt in the sample= $[A*V_{ext}/1000]*[100/Ws]$ where;

A : salt concentration(mg/l)= 640*EC (mmhos cm^{-1})

V_{ext} : volume of the extract solution (ml)

Ws: Weight of sample (mg)

2.4.3.2 Qualitative Analysis of the Soluble Salts by Spot Tests

The salt extract solutions were later concentrated by evaporation in oven at 40^0C for 6 hours. The most common soluble salts in the porous building materials are sulphates, chlorides, nitrates, nitrites and phosphates of sodium, potassium and magnesium elements. The qualitative spot tests indicate their presence and possible sources. Here only anions were tested as follows.

Determination of PO_4^{-3} Ions : A drop of test solution was placed on a filter paper. A drop of ammonium molibdate ($(NH_4)_2MoO_4$) solution was added. The filter paper was held over a hot wire gauze or near a bunsen burner to accelerate the reaction. Then a drop of benzidine reagent was added and the paper was held over ammonia. The formation of a blue fleck or ring is due to presence of phosphate ions. Limit of identification of the test is 1.25 microgram as P_2O_5 (Feigl, 1958).

Determination of SO_4^{-2} Ions : A drop of the test solution was placed in a test tube. Then 1 or 2 drops of 2M hydrochloric acid and 1 or 2 drops of a 10% solution of barium chloride ($BaCl_2$) are added. Formation of white precipitate is due to sulphate ions (Teutonico,1988).

Determination of Cl^- Ions : A drop of test solution was placed in a test tube and 1 or 2 drops of dilute nitric acid and 1 or 2 drops of silver nitrate solution ($AgNO_3$ 0,1M) were added. Formation of a white gelatinous precipitate indicates the presence of chloride ions (Teutonico,1988). Limit of identification of the test is 0.3 microgram as chlorine (Cl) (Feigl, 1958).

Determination of Nitrite NO_2^{--} Ions : A drop of test solution was placed on a spot plate. A drop of sulfanilic acid and α-naphthylamine solutions were added. Formation of a red-pink colour indicates of nitrite ions (Teutonico,1988). Limit of identification of the test is 0.04 microgram as nitrous acid (HNO_2) (Feigl, 1958).

Determination of Nitrate NO_3^- Ions : A drop of test solution was placed on a spot plate. A drop of, 2M acetic acid, sulfanilic acid, α-naphytlamine and a few mg of zinc dust were added. The formation of a red colour indicates the presence of nitrate ions (Teutonico,1988). Limit of identification of the test is 0.05 microgram as nitric acid (HNO_3) (Feigl, 1958).

Determination of Carbonate CO_3^{-2} Ions : A drop of test solution was placed in a test tube. One or two drops of 4M hydrochloric acid were added. The appearance of bubbles of gas (CO_2) indicate the presence of carbonate ions (Teutonico,1988).

2.4.4 Examination of Pozzolanic Activity of the Fine Aggregates

One of the durability related experiments is the test for pozzolanic activity. Pozzolanic activity shows the abundance of pozzolanic aggregates. Pozzolanic activity of the aggregates of some plasters was determined using a method that is the modification of the methods given by Luxan, 1989; TS EN 196-5, 2002 and Suzuki et al., 1985.

For this test, 0.05g of aggregates having sizes <125µ, and the ones on 125µ sieve were used.

0.05 g of aggregates were put in containers filled with 30 ml saturated $Ca(OH)_2$ solution and covered. To some containers, only saturated $Ca(OH)_2$ was added to be measured as blank. All containers were left covered for 10 days. After that 10 ml of solution from each container was taken and titrated with 0.01M EDTA. EDTA solution was standardized with pure $Ca(OH)_2$. Indicator used was calcon in all titrations. In order to keep the pH at 12-13, 10% NaOH solution was used (Black, 1965).

The differences in concentration of Ca^{2+} ion between the sample solutions and blank solution can be obtained from the results of titration. Since pozzolanic active aggregate reacts with Ca^{2+} ion, the differences in the concentration of Ca^{2+} ion gives the information about the pozzolanic activity of the aggregates for ten days of reaction period. In order to make comparison of that activity with the literature values, where the drop in Ca^{2+} ion concentration was calculated for 25g of sample aggregate in a liter of saturated $Ca(OH)_2$ solution and expressed as drop in electrical conductivity (Luxan et. al, 1989), the values obtained for 0.05g of aggregate in 30 ml of saturated $Ca(OH)_2$ solution were expressed for 25g of sample aggregate in a liter of saturated $Ca(OH)_2$ solution.

In Luxan et al, 1989, the consumption of $Ca(OH)_2$ was measured as drop in electrical conductivity. In the present study, the consumption of $Ca(OH)_2$ was converted to drop in electrical conductivity by the simple equation given below; (Black, 1965).

Total cation concentration, me per liter = 10 x (the electrical conductivity in mmho)

Where; total cation concentration corresponds to concentration of Ca^{2+} ion consumed.

2.4.5 Analysis of Pozzolanic Reaction Products by Recrystallization

In order to verify the formation of calcium silicate hydrate as a pozzolanic reaction product in the plasters and to make its mineral identification, a new test was established.

Fine aggregate portions (<125µ and 125µ) of six plasters were left in saturated $Ca(OH)_2$ solution for four weeks. After that time, they were examined under microscope and their XRD patterns were taken for mineral identification (Shi, 1998).

2.4.6 Mineralogical Properties of Plasters

Mineralogical properties of plasters were examined by using thin section analysis, SEM-EDX, XRD, FTIR, and TGA analyses.

2.4.6.1 Thin Section Analysis

For this analysis samples were placed into plastic molding boxes of 1.5x3x1cm. They were saturated with the polyester (ESKIM- extra POLYESTER) mixed with accelerator and hardener under vacuum of 100 torr. Following their hardening, the molded samples were removed from boxes and cut into 1mm slices to be fixed and reduced to 30µ thickness on microscope slides. Thin sections of the samples were examined using polarizing microscopes of Nikon AFX-2A and Carl Zeiss equipped with a photographic attachments. Mineralogical and morphological properties of binder and aggregates, such as shape, size, and distribution of particles in the matrix were examined.

2.4.6.2 Scanning Electron Microscopy (SEM) Coupled With Energy Dispersive Analyzer (EDX)

SEM analysis aimed to provide complementary information about morphology and microstructure of binder and aggregate parts and possible reaction products formed among the binder and aggregate. Plaster pieces of about 0.5 cm dimensions with at least one flat surface was prepared and coated with gold. The instrument used was a JEOL JSM-5400 Scanning Electron Microscope operated at 22 kV and coupled with Energy Dispersive X-ray analysis (EDX) system by which elemental analysis can be done.

SEM micrographs were taken where possible and elemental analyses were carried out and evaluated together with the micrographs.

2.4.6.3 X-Ray Diffraction (XRD) Analyses

X-ray diffraction analyses were carried out on powdered plaster samples. Before the analyses, layers of plasters were separated and each layer was ground in an agate mortar. Some ground samples were treated with 2% aqueous solution of acetic acid (CH_3CO_2H) to dissolve all $CaCO_3$. After CO_2 gas evolution ceased, the mixture was washed with distilled water several times. After decantation, centrifuge tubes with samples in them were dried in an oven at about 40^0C. Then the XRD analyses of the samples were carried out using unoriented mounts.

The instrument used was a Philips type PW1352/20 X-ray diffractometer. Analysis was done using CoKα radiation with Ni filter, adjusted to 35kV and 14mA. The XRD traces were recorded for the 2θ values from about 6^o to 75^0. Mineral phases were identified in XRD traces.

2.4.6.4 Termogravimetric Analysis (TGA)

Termogravimetric analysis was carried out in some samples in order to understand if the organic matter was present and what its percentage was through the weight changes on heating. Powdered samples were analyzed using the instrument of General V4.1C.DuPont 2000.

2.4.6.5 Fourier Transform Infrared Spectroscopic Analysis (FTIR)

In order to support the results obtained by other methods for mineral composition, pigment layer of fresco plasters were also analyzed by FTIR. The analyses were carried out with a Mattson 1000 FTIR spectrometer for the characteristic absorption bands between 500-4000cm^{-1}. Samples were prepared by making homogeneous mixture with pure KBr and very small amount of powdered sample and pressing to pellets to be observed in FTIR instrument..

2.5 Preparation of New Plaster Samples

In order to have an idea about the effects of aggregates on the ultrasonic velocity, thus on the mechanical properties of plasters, some new plasters were prepared with the original aggregates of a sample (KSP4) and some others with the quartz aggregates. These new plasters are described in the following Table.

Table 2.1 Description of New Plasters Prepared

Sample	Type of Aggregates	Particle Size of Aggregates	Binder: Aggregate Ratio
K1	Original aggregates of sample KSP4	<125µ	40% aggregate 60% binder
Q1	Quartz aggregates	<125µ	40% aggregate 60% binder
K2	Original aggregates of sample KSP4	125µ	40% aggregate 60% binder
Q2	Quartz aggregates	125µ	40% aggregate 60% binder

CHAPTER III

EXPERIMENTAL RESULTS

Results of various analyses carried on plaster samples are given under the titles of the experiments, in the following sections of this chapter. Discussions of those experimental results and the final conclusions are given in Chapters IV and respectively.

3.1 Basic Physical Properties of Plasters

Basic physical properties of plasters as bulk density, porosity, water absorption capacity and water vapour permeability are given in two subsections.

3.1.1 Bulk Density, Porosity and Water Absorption Capacity

Although the bulk density and porosity values of plaster samples showed some differences in one to the other, they were all low density and high porosity plasters (Figure 3.1, Appendix 8).

The density of the samples varied in the range of 1.23 gr/cm^3-1.90 gr/cm^3, the average being 1.49 gr/cm^3. Average density of Kubadabad Samples seemed to be lower than the average, being around 1.39 g/cm^3.

The porosity of the samples varied in the range of 19.67%-49.03%, the average being 38.34%. As it is expected, samples of lower density have higher porosity, and vice versa. The lowest density ALP5 1.23 gr/cm^3 corresponds to high porosity of about 49.0%, and highest density (ŞKP1, 1.90 gr/cm^3) corresponds to the lowest 19.7% porosity as expected.(Fig.3.1).

Water absorption capacity values of the plasters varied in the range of 10.3%-39.8%, the average being 26.7% (Appendix.8).

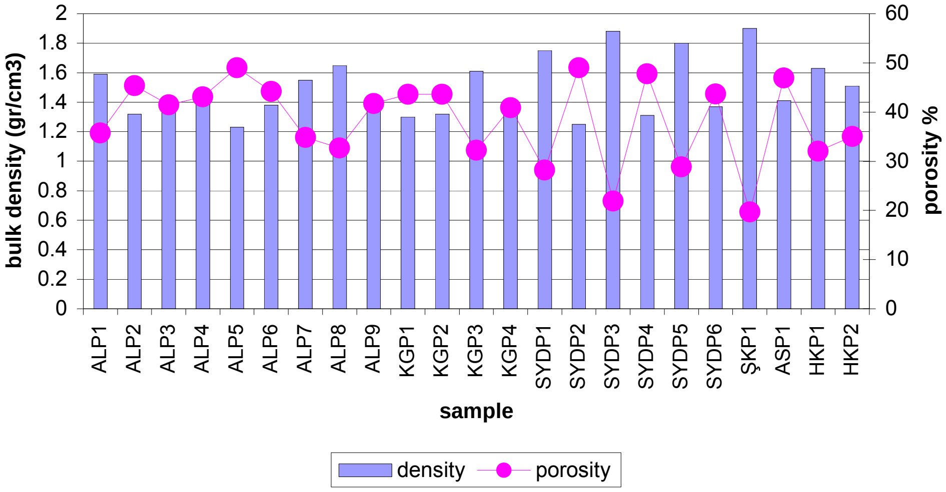


Fig.3.1 Bulk Density and Porosity Values of Plasters

3.1.2 Water Vapour Permeability of Plasters

The water vapour permeability properties of the plasters were measured as explained in section 2.1.2, and expressed as equivalent air thickness of water vapour permeability (SD), which was calculated for a known thickness of the sample. Water vapour diffusion resistance coefficient (μ) was calculated by dividing SD with the thickness of the sample. The results obtained were given in Table 3.1.

As it is seen from the table, μ values of the plasters ranges from 1.79 to 9.22. Although, the real thickness of the plasters on the walls are not very well known, an approximation was made that the thicknesses of the samples are the same as the original thicknesses. Therefore, SD values of the plasters could be compared. SD value of plasters ranges from 0.020m to 0.069m.

Table 3.1 Water Vapour Diffusion Resistance Coefficient (μ) and SD values of Plasters

Sample	μ	SD (m)
ALP1	3.82	0.028
ALP2	3.66	0.053
ALP3	4.13	0.055
ALP4	9.22	0.049
ALP5	2.31	0.031
ALP6	2.29	0.034
ALP7	6.38	0.069
ALP8	3.83	0.054
ALP9	1.79	0.039
SYDP1	7.84	0.046
SYDP2	2.06	0.020
SYDP4	3.37	0.037
SYDP5	4.65	0.049
KGP2	3.18	0.068
KSP4	2.73	0.037

3.2 Basic Mechanical Properties of Plasters

The test related with mechanical properties of plasters was ultrasonic pulse velocity measurements. They were used to calculate modulus of elasticity (E_{mod}). Since the samples were mostly in small size and rather friable, other mechanical tests such as the tests for uniaxial compressive strength could not be carried out.

3.2.1 Modulus of Elasticity

Modulus of Elasticity of plasters was calculated according to the method given in section **2.3.1.** E_{mod} of plaster samples was found to be in the range of 1072 Mpa-5583 Mpa, average being 2855 MPa. (Figure 3.2, Appendix 9). More than half of the plasters have E_{mod} values between (2000-3000)Mpa The plasters of Kubadabad Great and Small Palaces seem to have similar mechanical properties and relatively high E_{mod} values. E_{mod} values of Alanya Castle samples show great variation. For example ALP4.2 has a low E_{mod} (452 MPa),but another sample ALP6.2 has a high value (5482 MPa).

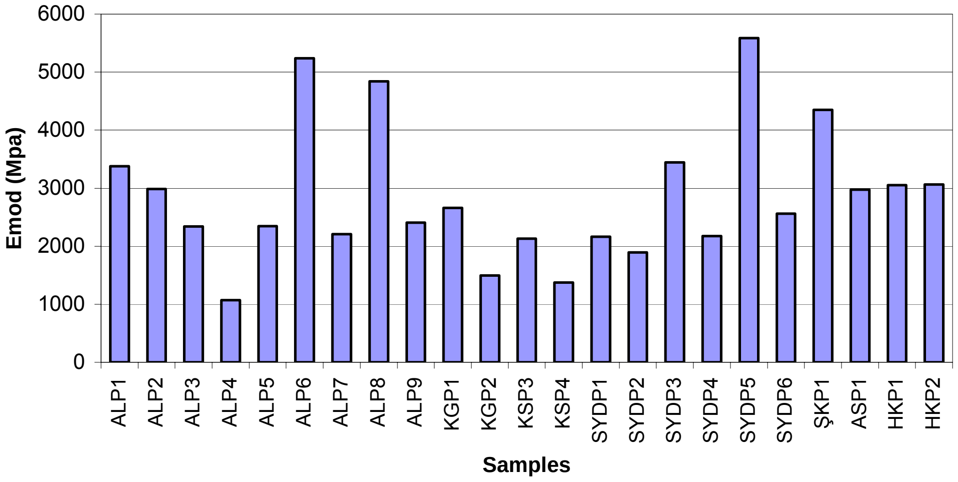


Fig.3.2 Modulus of Elasticity Values of Plasters

3.3 Determination of Raw Material Properties

Raw material properties of plasters were determined by the experiments on the amounts of binder and aggregate parts by acid treatment and by volumetric method, particle size distribution of aggregates, quantitative and qualitative analyses of soluble salts in plasters, examination of pozzolanic activity of fine aggregates, analysis of pozzolanic reaction products by recrystallization experiments and finally the mineralogical properties using several analytical techniques.

3.3.1 Proportions of Binder and Aggregate Parts

The proportions of binder and aggregate parts were determined by treatment with acid, weighing the acid insoluble part and by the volumetric titration of the Ca^{2+}ion in the acid soluble part as described in 2.4.1.

3.3.1.1 Proportions of Binder and Aggregate Parts by Acid Treatment

The results have shown that the amount of binder $CaCO_3$ was high being in the range of 53.8%-96.8%, the average being 85.3%.
Lime content of the majority of the samples was above 80%. Some exceptions were SYDP1 60.3%, KSP4 59.0% and SYDP3 53.8%. Those samples were the rough plaster layers which had higher amount of aggregates. In fact, the remaining plasters studied were fine plaster layers. The binder contents of the samples are given in Figure 3.3 and in Appendix 10.

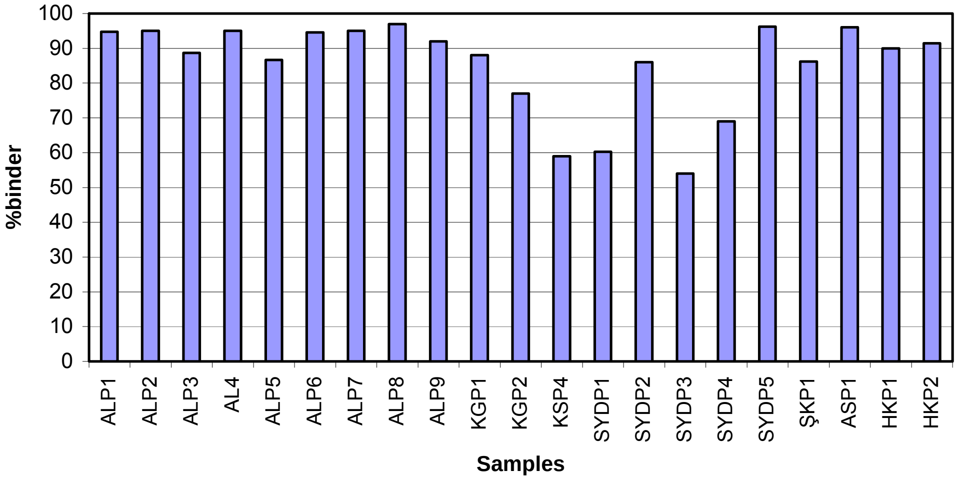


Fig. 3.3 Binder Content (%) of the Plasters

3.3.1.2 Determination of Binder and Aggregate Parts by Volumetric Titration Method

The proportion of lime binder was also determined using complex formation titration with EDTA standard solution as described in 2.4.1.2. This test only gives amount of Ca^{2+}ion, which was used to calculate the amount of $CaCO_3$ in the plasters. Comparison of the results with the those of previous section 3.3.1.1 has indicated the presence of other carbonates such as dolomite since the average amount of $CaCO_3$ with this method was found to be 78.7% instead of 85.3 % which was obtained through weight loss by acid treatment. The results are given in Table 3.2.

Table 3.2 Percentage of $CaCO_3$ Obtained from Titration Method

Sample	**% $CaCO_3$***
ALP1	71
ALP2	91
ALP5	82
ALP6	74
ALP8	89
KGP1	80
KSP4 (fine layer)	86
KSP4 (rough layer)	54
HKP2	81

*Results are the average of at least two titrations.

3.3.2 Particle Size Distribution of Aggregates

Aggregate parts of plasters were divided into five groups using the sieves of open diameters as 125μm, 250μm, 500μm and 1000μm.

Particle size distribution of the samples were given in Figure 3.4 (Appendix 11). Aggregates can be classified according to their average grain size. (Tucker, 1991). Applying Udden and Wentworth scale, aggregates were named by size of the highest percentage aggregates in the sample. If the highest percentage of aggregates have the size ≤250µ, then the aggregate is called fine aggregate. Thus ALP1, ALP3, ALP5, ALP6, ALP9, SYDP2, SYDP5 samples are plasters having fine aggregates. If weight percent of aggregates having size ≥500µ is the highest percentage, then the aggregate is called coarse aggregate. Thus ALP2, ALP7, KGP1, KGP4, SYDP3, HKP1, HKP2 are plasters having coarse aggregates.. If the distribution of aggregates is almost even, the sample can be named as mixed aggregate. For example ALP4, ALP8, KGP2, SYDP1, SYDP4, ŞKP1 are the plasters having mixed aggregates.

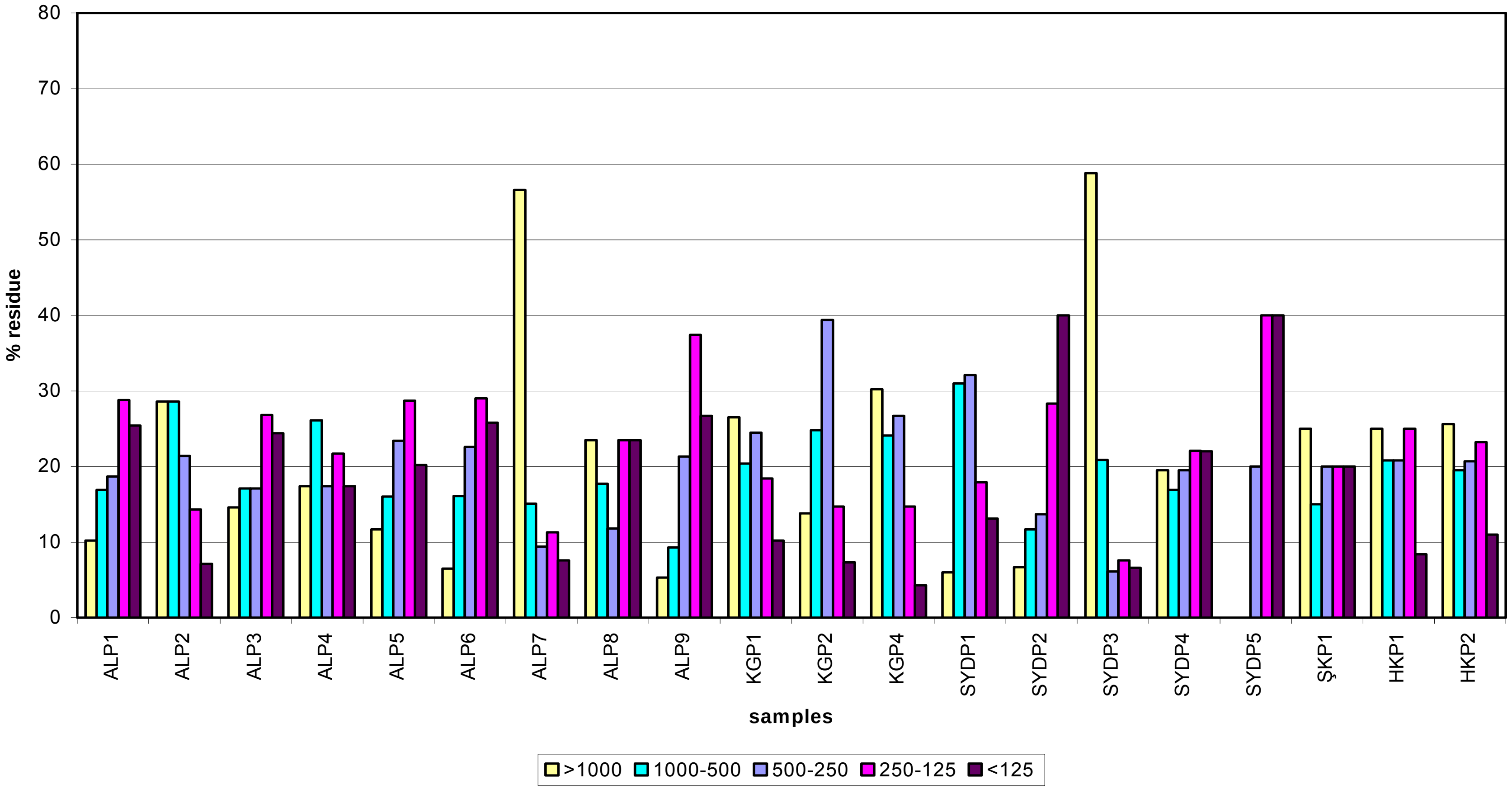


Fig. 3.4 Particle Size Distribution of Aggregate

3.3.3 Soluble Salt Content

The soluble salt contents of the plasters were in the range of 0.12%-2.43% by weight (Table 3.3). ALP1(2.43%) and ALP8(2.31%) contained relatively high amount of soluble salt. Except these two samples, soluble salt content of all plasters varied between 0.12%-0.55%, the average being 0.46%.

Table 3.3 Soluble Salt Content (%) and Results of Spot Test Analysis

Sample	**%Salt**	**PO_4^{-3}**	**SO_4^{-2}**	**Cl^-**	**NO_2^-**	**NO_3^-**	**CO_3^{-2}**
ALP1	2.43	-	+	+	+	+	-
ALP2	0.26	+	-	-	+	+	-
ALP3	0.27	-	-	-	-	+	-
ALP4	0.29	-	-	+	+	+	-
ALP5	0.47	+	-	+	+	+	+
ALP6	0.13	-	-	-	+	+	-
ALP7	0.25	+	-	-	-	+	+
ALP8	2.31	+	-	+	+	+	-
ALP9	0.55	+	+	+	+	+	-
KGP1	0.14	+	+	-	+	+	+
KGP2	0.12	+	+	-	+	+	+
KGP4	0.13	+	+	-	+	+	+
SYDP1	0.15	+	-	-	-	+	-
SYDP2	0.17	+	-	-	-	+	+
SYDP3	0.39	+	-	-	-	+	+
SYDP4	0.21	+	-	-	-	+	-
SYDP6	0.32	+	-	-	-	+	+
ASP1	0.23	+	-	-	+	+	+
ŞKP1	0.15	+	-	-	+	+	-
HKP1	0.14	+	-	-	+	+	-
HKP2	0.55	+	-	+	+	+	-

3.3.4 Spot Test Analysis of the Soluble Salts in the Plasters

All plaster samples have the soluble salts having nitrate ion as the anion. The sources of nitrate ions might be the earth or decomposition of nitrogenous organic matters and atmospheric pollutants (Teutonico, 1988; Shaffer, 1972). Phosphate is another common ion identified in the samples. Almost all samples (except ALP1, ALP3, ALP4, ALP6) contain phosphate ions. Sulphate was detected only in five samples, two of them belonging to Alanya. On the other hand, all Kubadabad samples contained sulphate ion which may come from soil of that location or from pollution. The results of spot test analysis of the samples are given in Table 3.3.

3.3.5 Examination of Pozzolanic Activity of Fine Aggregates

Pozzolanic activity of the aggregates are presented in Table.3.4. The calculation of pozzolanic activity was done as described in section 2.4.6.
According to results obtained, the finest sized aggregates (< 125 μ) of Alanya Byzantine Plaster ALP4 have the highest activity being 42 mS/cm whereas Kubadabad Great Palace Plaster KGP2 aggregates of 125μ size has the lowest activity being 0.9 mS/cm. However, the finest sized aggregates (< 125 μ) of the same sample has the activity as 4.2 mS/cm which is good pozzolanicity since the pozzolanas having the values of greater than 1.2 mS/cm, considered as good pozzolanas (Luxan et. al., 1989). According to that classification, all the finest and finer aggregates of the plasters have very high pozzolanicity.
Regarding the particle size, the pozzolanic activity increases with decreasing particle size i. e., in ALP4, aggregates of < 125 μ size have the activity 42 mS/cm, and the aggregates of 125μ size have the activity 21 mS/cm.

Table 3.4 Results of the Test for the Pozzolanic Activity of Some Aggregates

Sample	**$Ca(OH)_2$ consumption (g) per 0.05 g material**	**ΔEC mS/cm**
ALP1 (<125µ)	0.0146	19.80
ALP1 (125µ)	0.0137	18.60
ALP4 (<125µ)	0.0311	42.00
ALP4 (125µ)	0.0155	21.00
ALP9 (<125µ)	0.0075	10.20
ALP9 (125µ)	0.0120	16.20
KGP2 (<125µ)	0.0031	4.20
KGP2 (125µ)	0.0006	0.90
SYDP4 (<125µ)	0.0066	9.00
SYDP4 (125µ)	0.0040	5.40
HKP2 (<125µ)	0.0042	5.70
HKP2 (125µ)	0.0042	5.70

3.3.6 Analysis of Pozzolanic Reaction Products on Fine Aggregates by Recrystallization

Fine aggregate portions (<125µ and 125µ) of six plasters, which were left in saturated $Ca(OH)_2$ solution for four weeks, were examined under microscope and their XRD patterns were taken for mineral identification.

A crystalline phase was formed on the aggregates, which was washed with distilled water, dried and photographed. The crystalline phase was also examined by XRD. The needle like crystals were observed under microscope (Fig. 3.5 a, b). XRD patterns of the crystals showed the presence of calcium silicate hydrate mineral, tobermorite (Figure 3.23). In addition, in one of the XRD patterns belonging to the aggregates of plaster ALP4, aragonite mineral beside calcium silicate hydrate was observed (Fig.3.23).

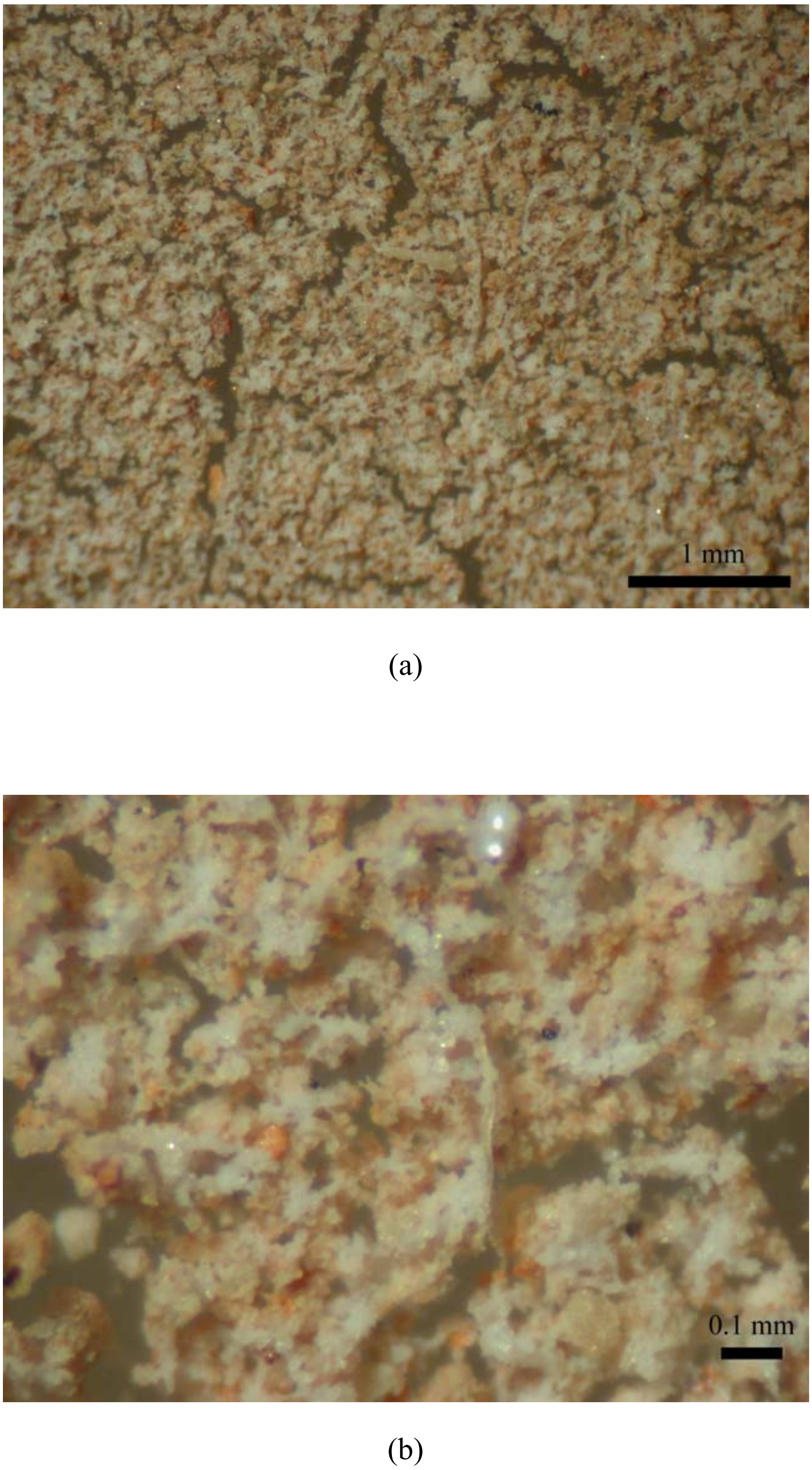


Fig. 3.5 Crystallization of tobermorite and aragonite on finest aggregates of ALP4 in saturated $Ca(OH)_2$ solution

3.3.7 Mineralogical Properties of Plasters

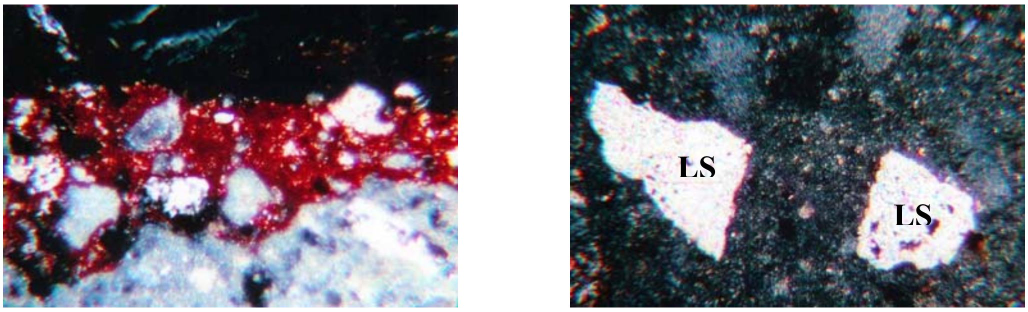
Mineralogical properties of plasters were studied by optical microscopic analysis of thin sections, SEM-EDX, XRD, TGA, and FTIR analyses to determine mineralogical phases and elemental compositions.

3.3.7.1 Thin Section Analysis

The petrographic analysis carried out on thin sections showed some common characteristics with respect to the matrix, which is mainly composed of micritic calcite with fine opaque minerals (Fig. 3.6b, 3.9, 3.7a.b). Some aggregates were observed in the matrix. They were limestone aggregates (Fig 3.6b), some silicate minerals like muscovite (Fig. 3.7a,b), pyroxene (Fig. 3.8a,b), and phillite (Fig. 3.8a,b). In the red colored and red zigzag decorated plasters micritic calcite and opaque minerals were also identified in the pigment layers (Fig. 3.6a, 3.10b,c, 3.12a,b).

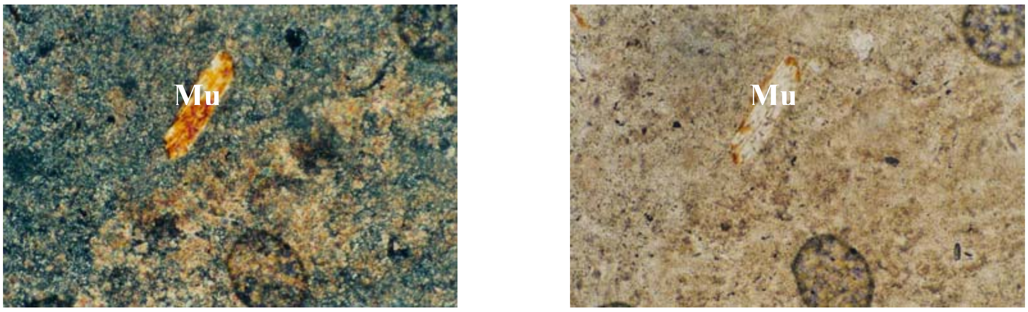
In thin sections very fine opaque minerals, which were identified as opal-A in XRD patterns, have appeared as perfectly mixed with lime binder (Fig. 3.6b, 3.9. 3.7a.b).

On the red zigzag decorated plaster samples haematite, calcite, sometimes dolomite and opaque minerals were observed. The particles appeared as well mixed in thin sections. This well mixing may be important in the hue and durability of the fresco colours.



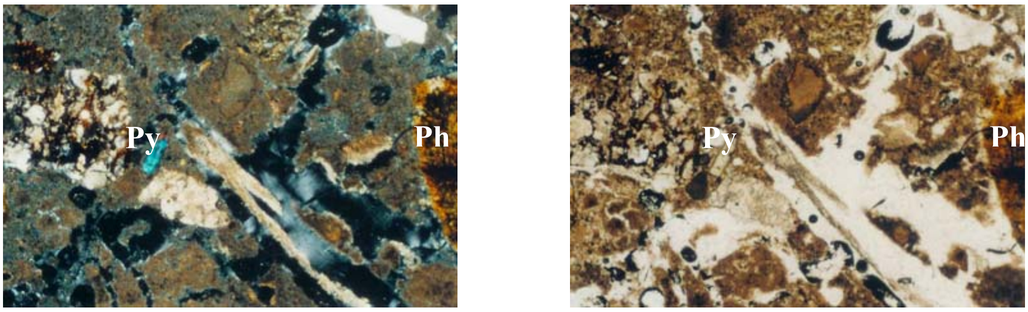
(a) (x100 cross nicols) (b) (x100 cross nicols)

Fig. 3.6 Alanya zigzag decorated Seljuk Plaster (ALP2)
LS: Limestone



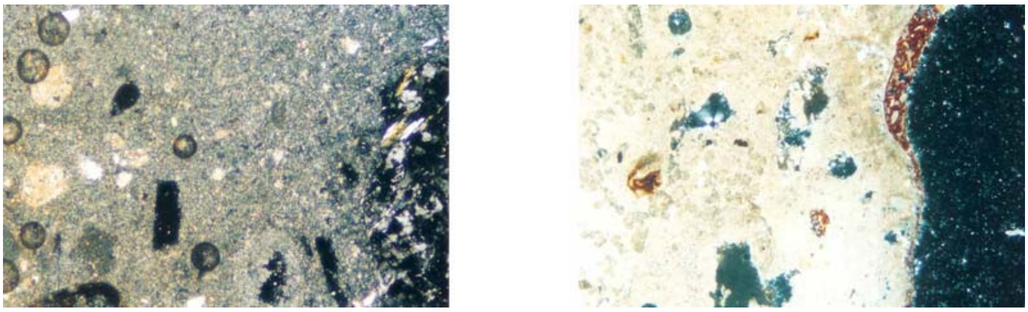
(a) (x200 cross nicols) (b) (x200)

Fig. 3.7 Alanya red colored Byzantine plaster (ALP4)
Mu: Muscovite



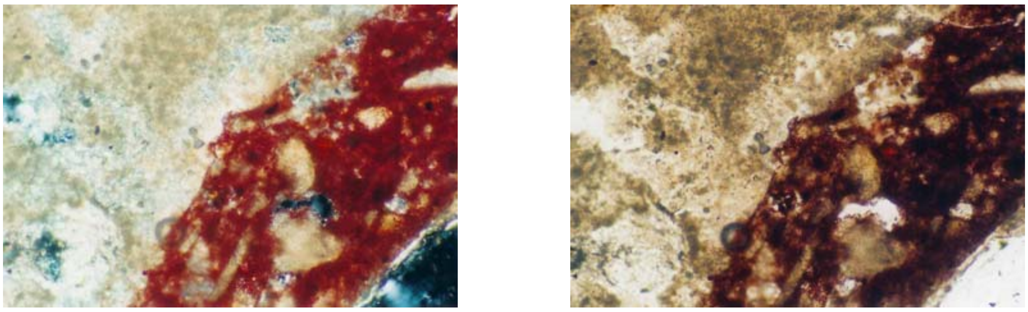
(a) (x40 cross nicols) (b) (x40)

Fig. 3.8 Kubadabad Small Palace Seljuk plaster (KSP4)
Py: Pyroxene, Ph: Phillite



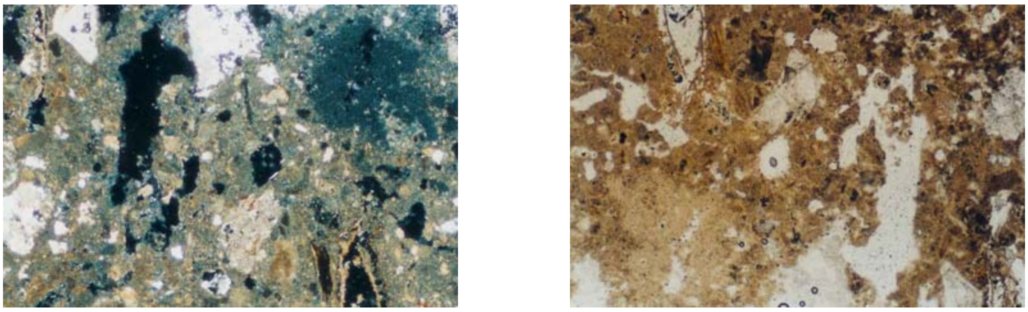
(x100 cross nicols) (a) (x25 cross nicols)

Fig 3.9 Syedra Byzantine Plaster (SYDP1)



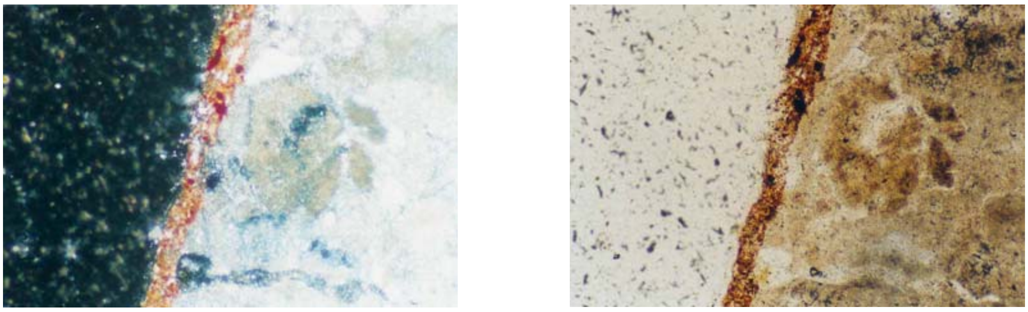
(b) (x200 cross nicols) (c) (x200)

Fig 3.10 Selinus-Şekerhane Köşk Seljuk red zigzag decorated plaster



(a) (x200 cross nicols) (b) (x200)

Fig 3.11 Hasbahçe Seljuk red zigzag decorated plaster



(a) (x40 cross nicols) (b) (x40)

Fig 3.12 Hasbahçe Seljuk red zigzag decorated plaster

3.3.7.2 SEM Analysis Coupled with EDX

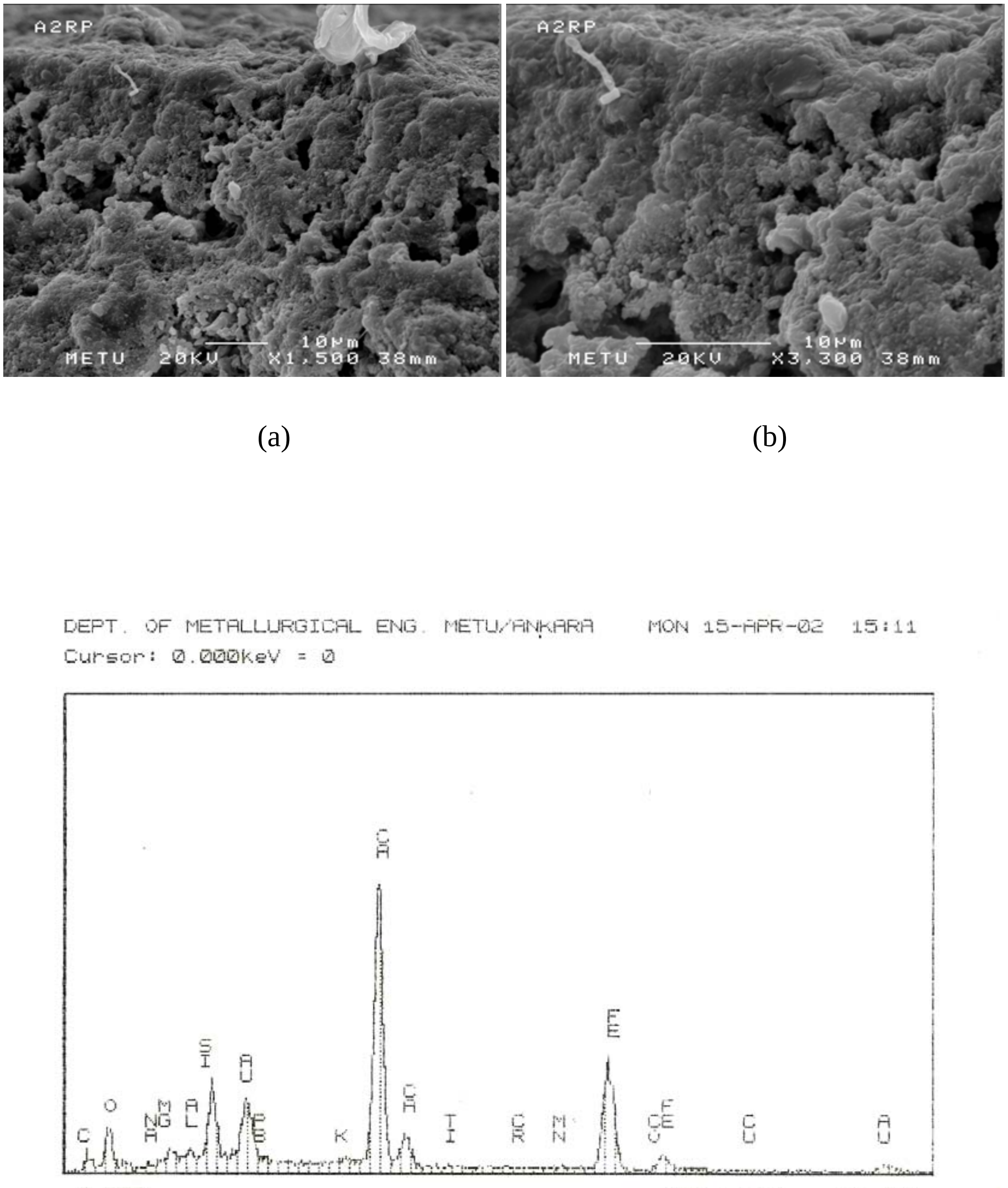
The SEM images of samples indicated that they are composed of micritic calcite crystals of size about 1μm together with very fine siliceous grains with the size less than 5μm (Fig. 3.17a,b). Those siliceous particles were identified as opal-A by XRD and TGA.

The pigment layer of plasters can be clearly distinguished from fine plaster layer due to size and porosity difference however, the pigment layer adhered well to the fine plaster layer proving that it was applied by using fresco technique. It means that powdered pigment mixed with water was applied on the wet lime plaster (Fig.3.13a,b, 3.15a, 3.16a).

In the SEM images of the sample that has highest pozzolanicity (ALP4) and interesting compact network structure, in comparison to more porous network of the others was observed (Fig. 3.15b, 3.16b, 3.18a,b, 3.19a,b). The structure could be the result of higher amount of pozzolanic products in the matrix (Shi, 1998)

Elemental analysis (EDX) of the matrix showed that beside main elements calcium and silicium, varying amounts of Al, Na, Mg, K are also present. These elements may be related with feldspars, dolomite, pyroxenes, clay minerals etc as aggregates (Fig. 3.16c, 3.17c, 3.18c, 3.19c).

The analysis of red colored and red zigzag coloured fresco samples show the presence of iron due to iron oxide (Fe_2O_3) (Fig.3.13c, 3.15c). The analysis of the green colored layer located below red color also showed the presence of iron but in much less amount (Fig. 3.16c). The green color might be due to the iron compound, iron being in lower oxidation state. The white colored base of the zigzag frescoes contained high amount of calcium (Fig.3.14 a, b, c).

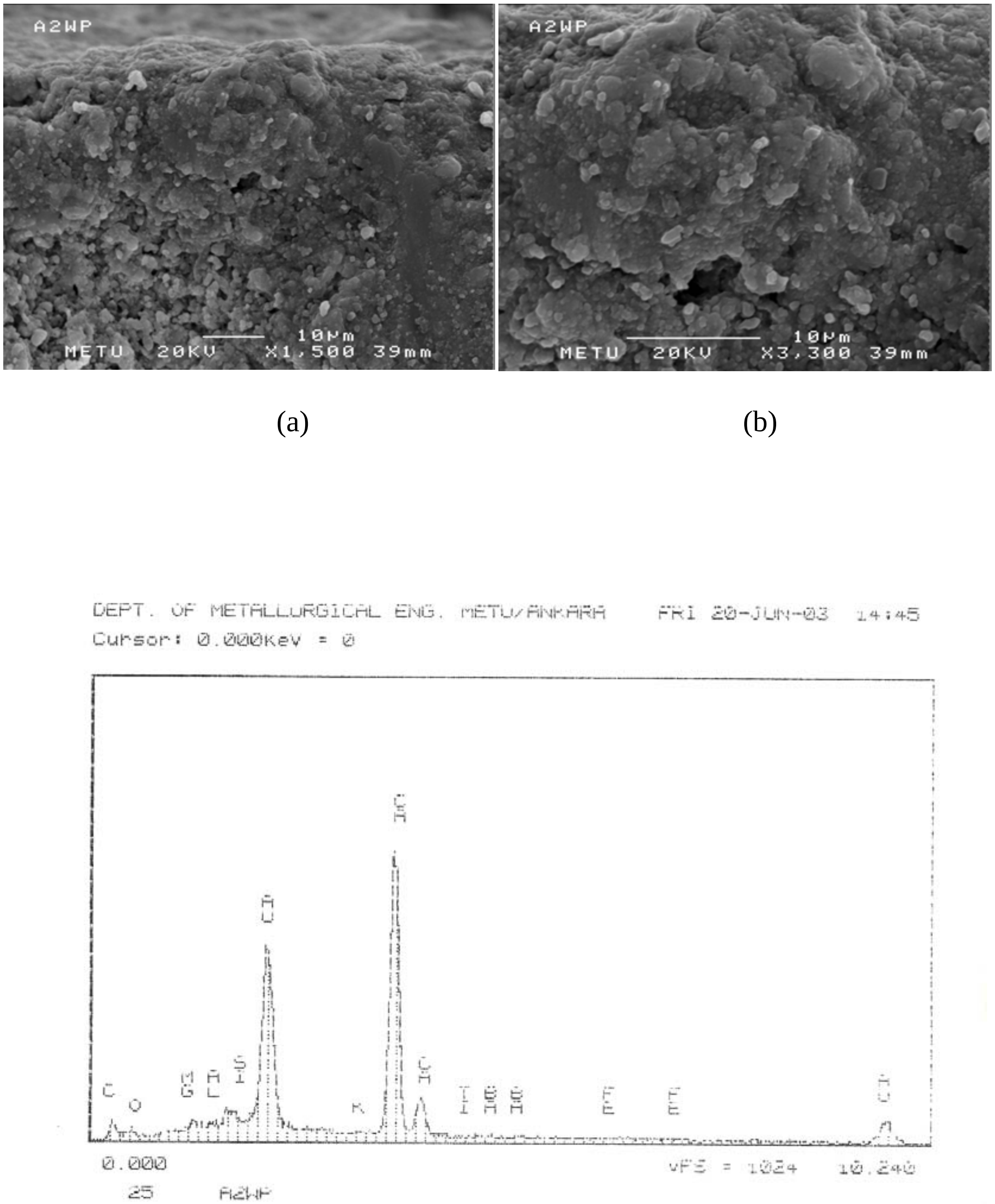


(a)

(b)

(c)

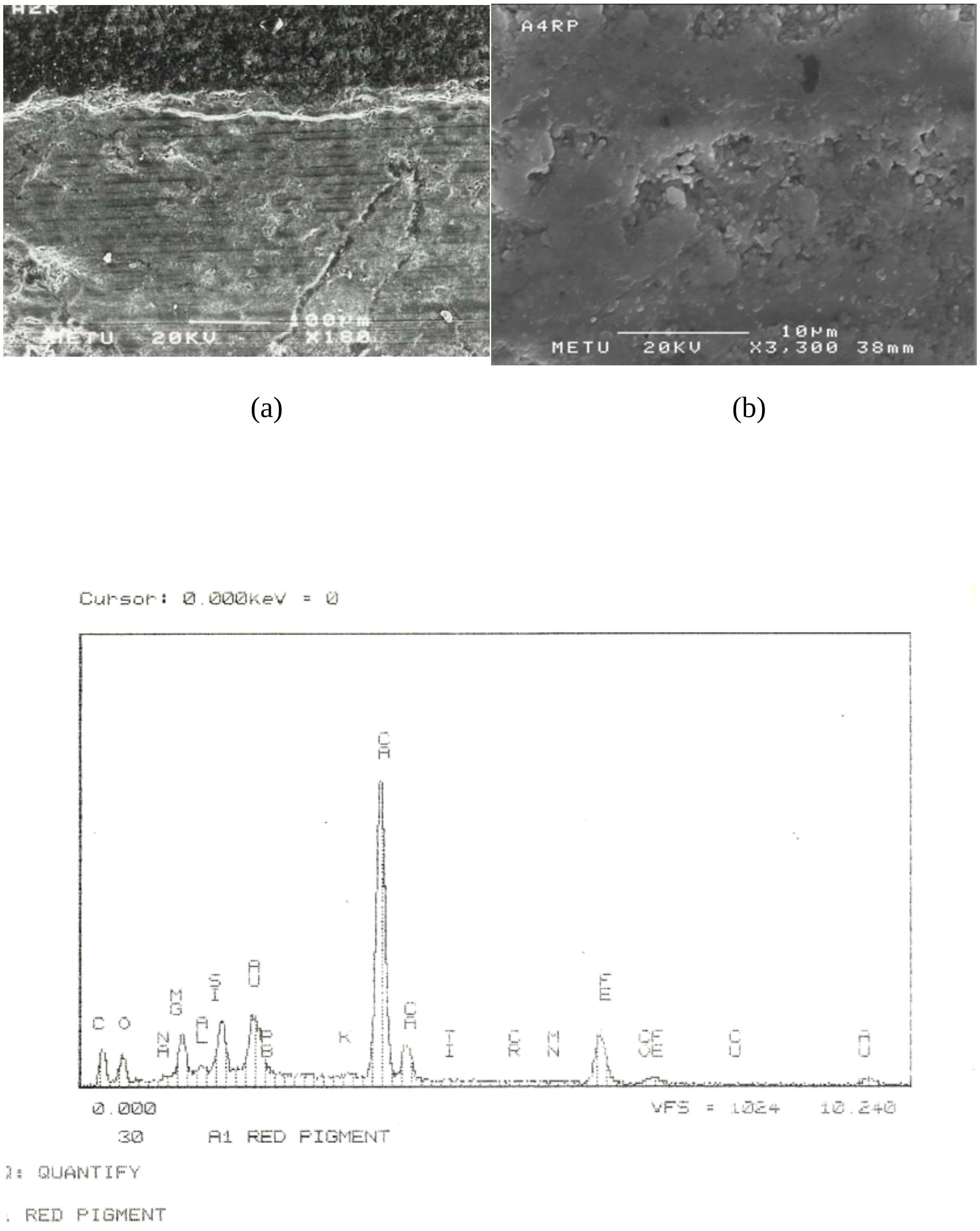
Fig. 3.13 SEM view (a, b) and EDX analysis (c) of the red pigment, Alanya Castle plaster (ALP2) (a; x1500, b; x3300)



(a) (b)

(c)

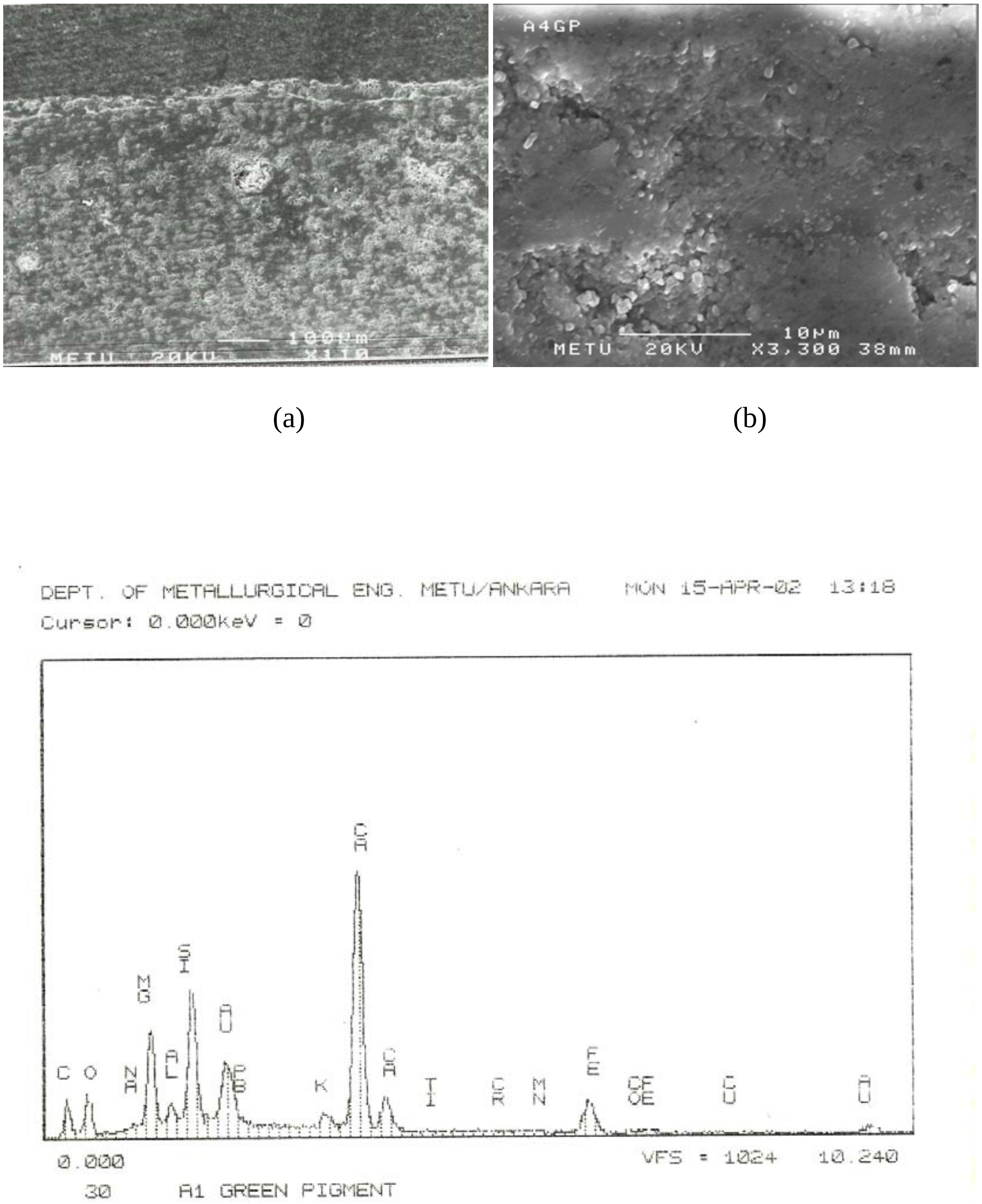
Fig 3.14 SEM view (a, b) and EDX analysis (c) of the white pigment, Alanya Castle plaster (ALP2) (a; x1500, b; x3300)



(a) (b)

(c)

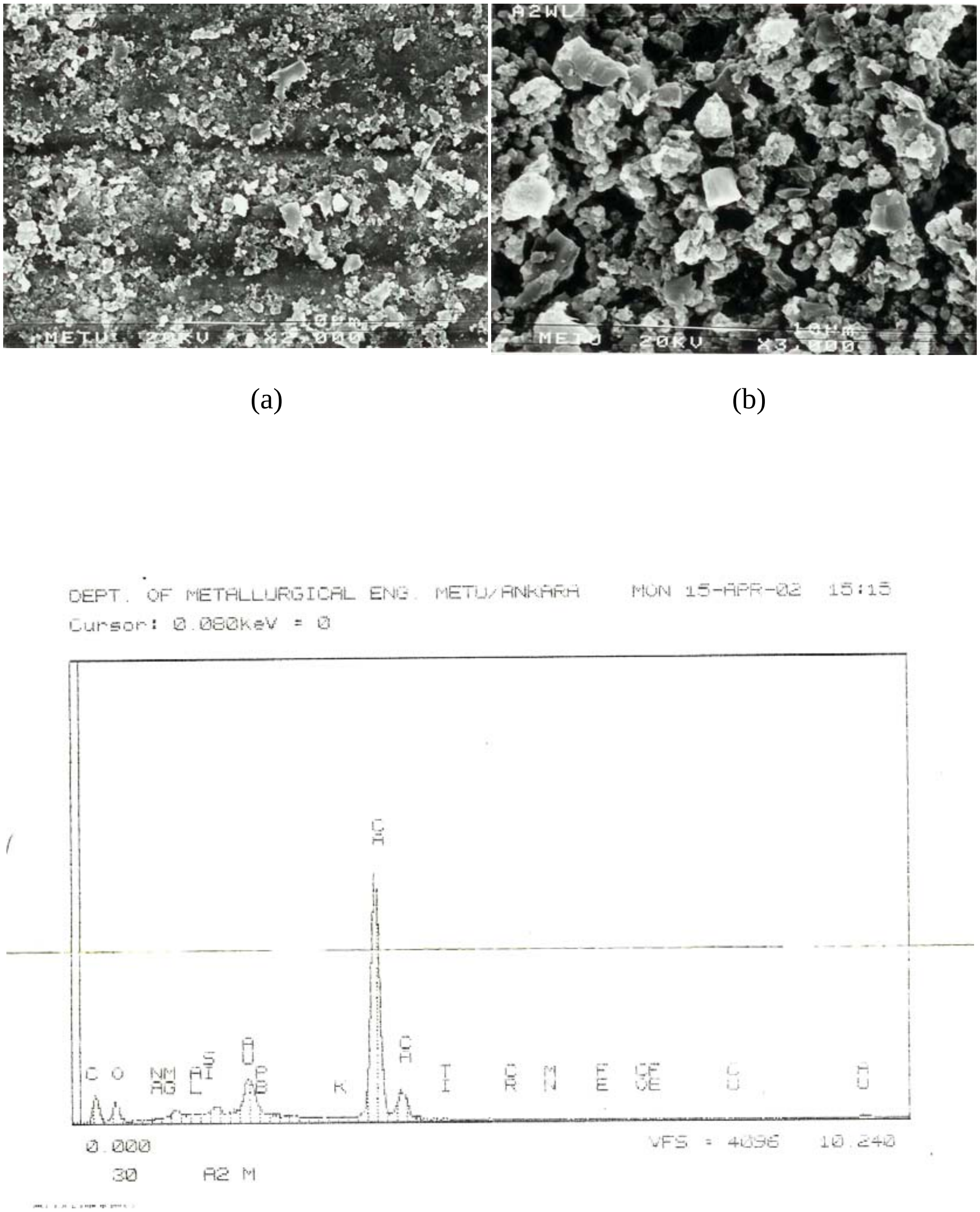
Fig 3.15 SEM view (a, b) and EDX analysis (c) of the red pigment, Alanya Castle plaster (ALP4) (a; x180, b; x3300)



(a) (b)

(c)

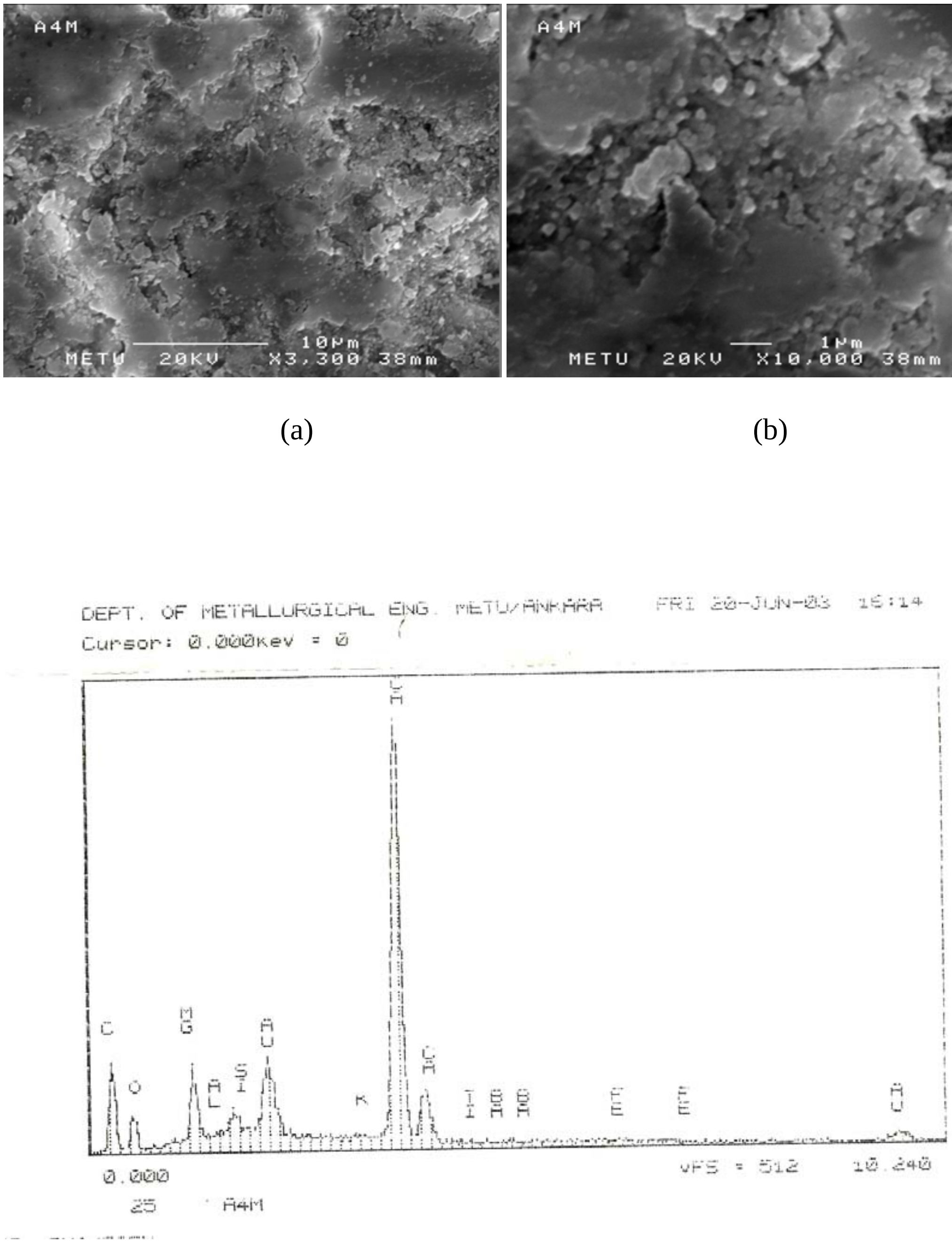
Fig 3.16 SEM view (a, b) and EDX analysis (c) of the green pigment, Alanya Castle plaster (ALP4) (a; x180, b; x3300)



(a) (b)

(c)

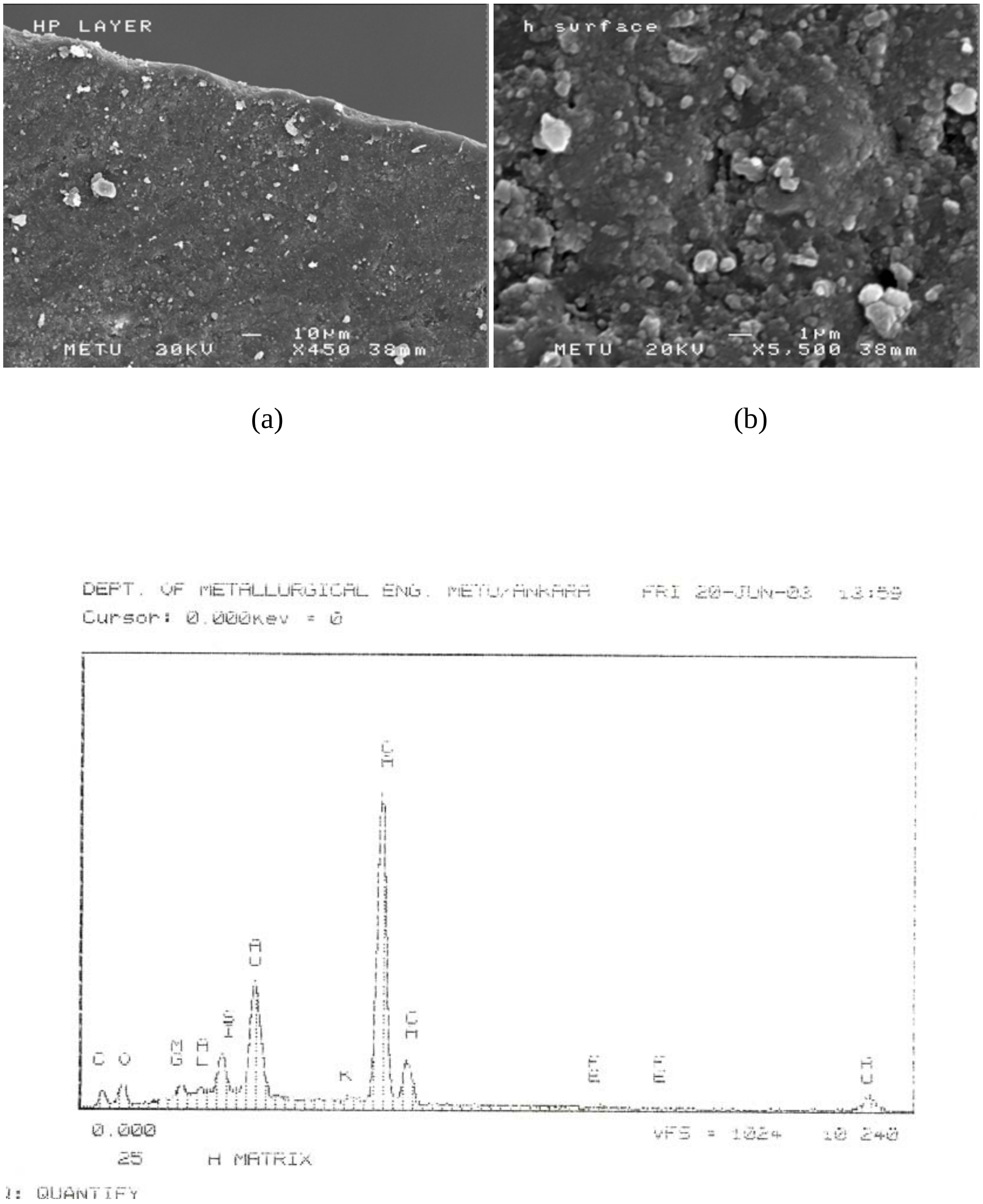
Fig 3.17 SEM view (a, b) and EDX analysis (c) of the plaster matrix, Alanya Castle (ALP2) (a; x2000, b; x3000)



(a) (b)

(c)

Fig 3.18 SEM view (a, b) and EDX analysis (c) of the plaster matrix, Alanya Castle (ALP4) (a; x3300, b; x10000)



(a) (b)

(c)

Fig 3.19 SEM view (a, b) and EDX analysis (c) of the plaster matrix, Hasbahçe plaster (HKP1) (a; x450, b; x5500)

3.3.7.3 X-Ray Diffraction Analysis

XRD analyses were carried out on all samples together with binder and aggregate parts, acid insoluble aggregates, pigment parts and acid treated pigment parts.

3.3.7.3.1 Analysis of Binder and Aggregates

XRD pattern of samples indicated that the main minerals of plaster layers are calcite and quartz. Beside these main minerals most of the samples had dolomite, feldspars, pyroxenes, Opal-A, opal-CT and some micas and chlorites. All Alanya fine plasters layers have calcite as the main mineral and some quartz. After treatment with 2% acetic acid, presence of minor amounts of dolomite became more evident as well as Opal-A. However, Opal-A seemed to be more in Byzantine fine plaster layer ALP4 (Fig.3.20).

Kubadabad plasters also have calcite as the main mineral. Acid treated aggregates reveal the presence of Opal-A, in all samples. Rough Kubadabad plasters are richer in minerals of feldspar, pyroxene and mica (Fig. 3.21).

Some bigger aggregates of Kubadabad rough plaster layers were separately analyzed by XRD. Yellow coloured aggregates prove to be quartz, whereas brown coloured aggregates contained mainly quartz with some pyroxene, feldspar and mica. They are the sedimentary aggregates of sandstone. (Fig.3.21). Syedra fine and rough plaster layers show the same characteristics that calcite was the main mineral with some quartz. The acid treatment was not done for these samples because of very small quantity of the samples. However, there are indications on the presence of Opal-CT (Fig. 3.22).

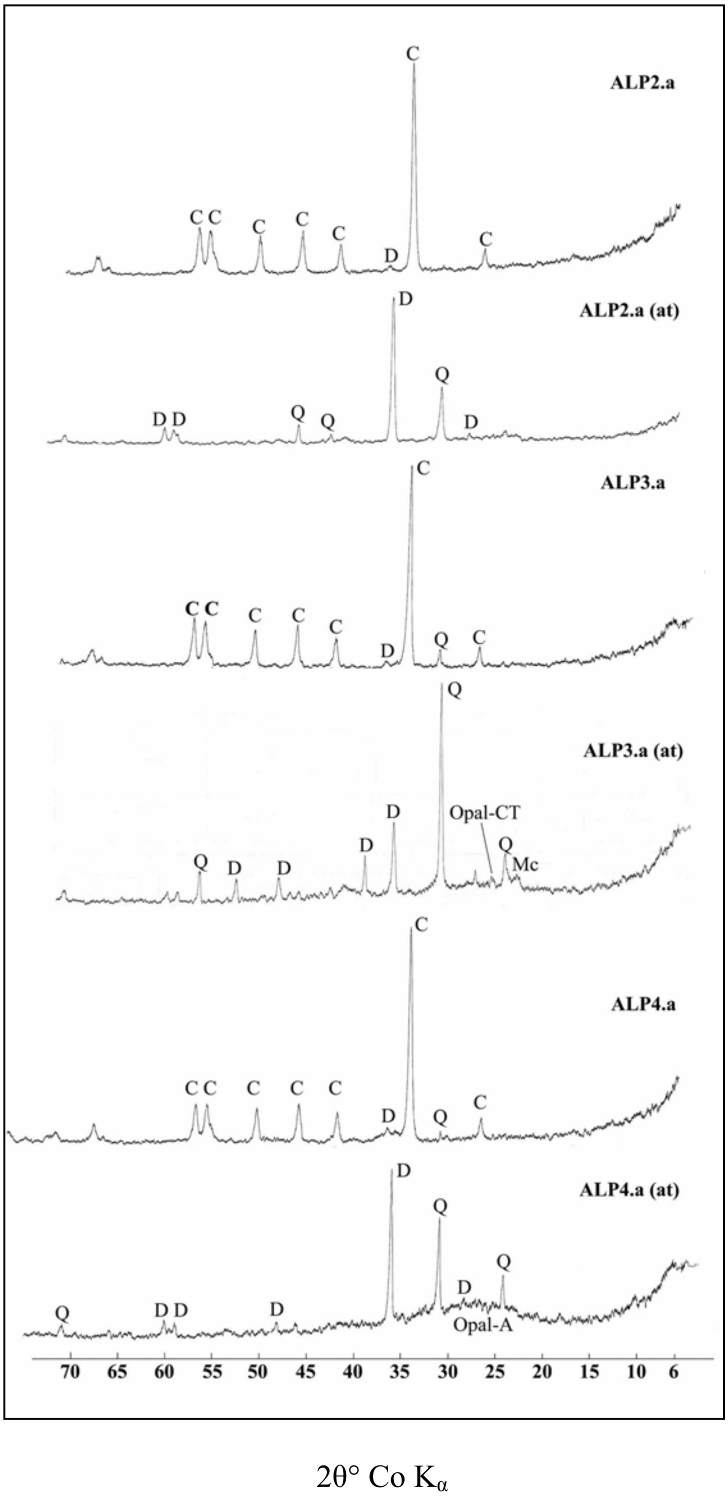


Fig. 3.20 XRD patterns of Alanya fine plaster layers
C: Calcite, D: Dolomite, Q: Quartz, Mc: Mica
at: 2% CH_3COOH treated.

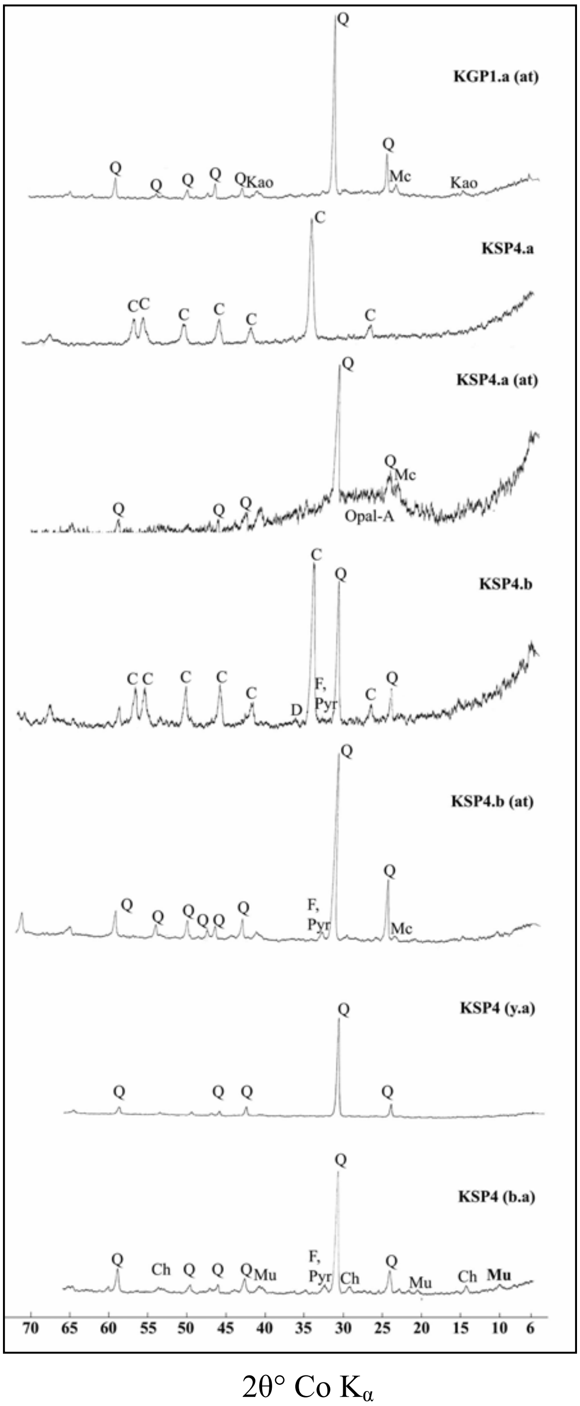


Fig. 3.21 XRD patterns of Kubadabad fine (a) and rough (b) plaster layers. KSP4 (y.a): XRD pattern of yellow colored aggregates, KSP4 (b.a): XRD pattern of brown colored aggregate. Notations are the same as given in Fig 3.20.
Kao: Kaolin, F: Feldspar, Py: Pyroxene, Mu: Muscovite, Cl: Chlorite

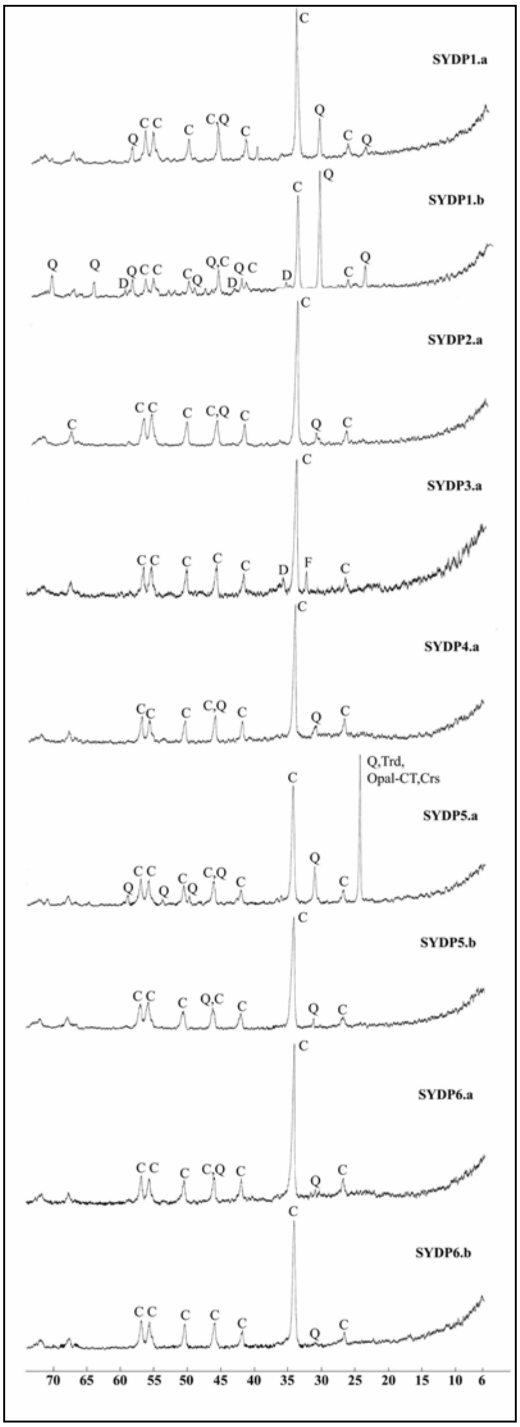


Fig. 3.22. XRD patterns of Syedra fine (a) and rough (b) plaster layers. Notations are the same as given in Fig 3.20.
Trd: Trydimite, Crs: Crystobalite

3.3.7.3.2 Analysis of Pigments

Among the samples studied, some samples are decorative and red zigzag patterned plasters. XRD analysis of these pigments layers indicated the presence of calcite and quartz clearly, but only one or two small peaks of haematite was seen. After treatment with 2% acetic acid, haematite was clearly identified. In all the red pigments analyzed, haematite was clearly seen after acid treatment. e.g. ALP2 rp, showed very small haematite peak, but acid treated form ALP2 rp(at) had intense haematite peaks (Fig.3.23) In addition, Opal-A was detected in all samples, which becomes more evident by acid treatment. In addition, dolomite was detected in all red pigment layers as a few percent (Fig. 3.23).

In the sample ALP4, green color was detected under the red pigment layer. The XRD pattern of it indicated that, celadonite may be responsible for the color, which is a silicate mineral containing iron with lower oxidation number.

XRD traces of finest aggregates (<125μ) belonging to plasters ALP1, HKP2 and ALP4, which were treated with saturated $Ca(OH)_2$ solution, showed the presence of tobermorite as newly crystallized mineral (Fig. 3.24). Tobermorite was together with aragonite in one sample ALP4. After acid treatment, the peaks of tobermorite and aragonite disappeared as expected (Fig.3.24).

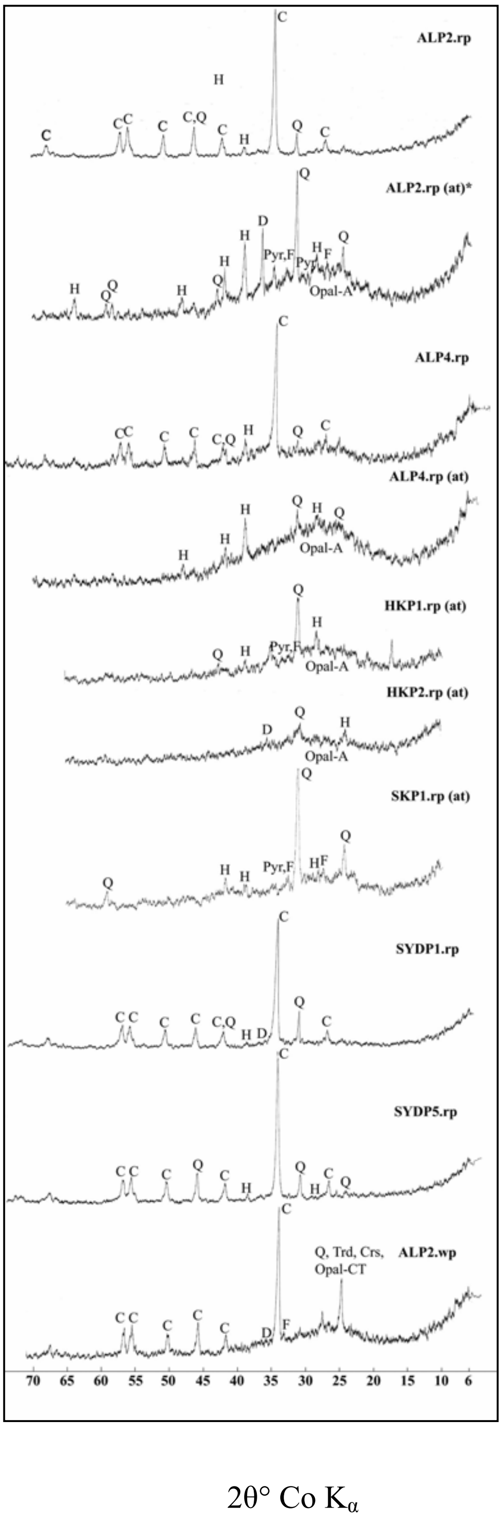
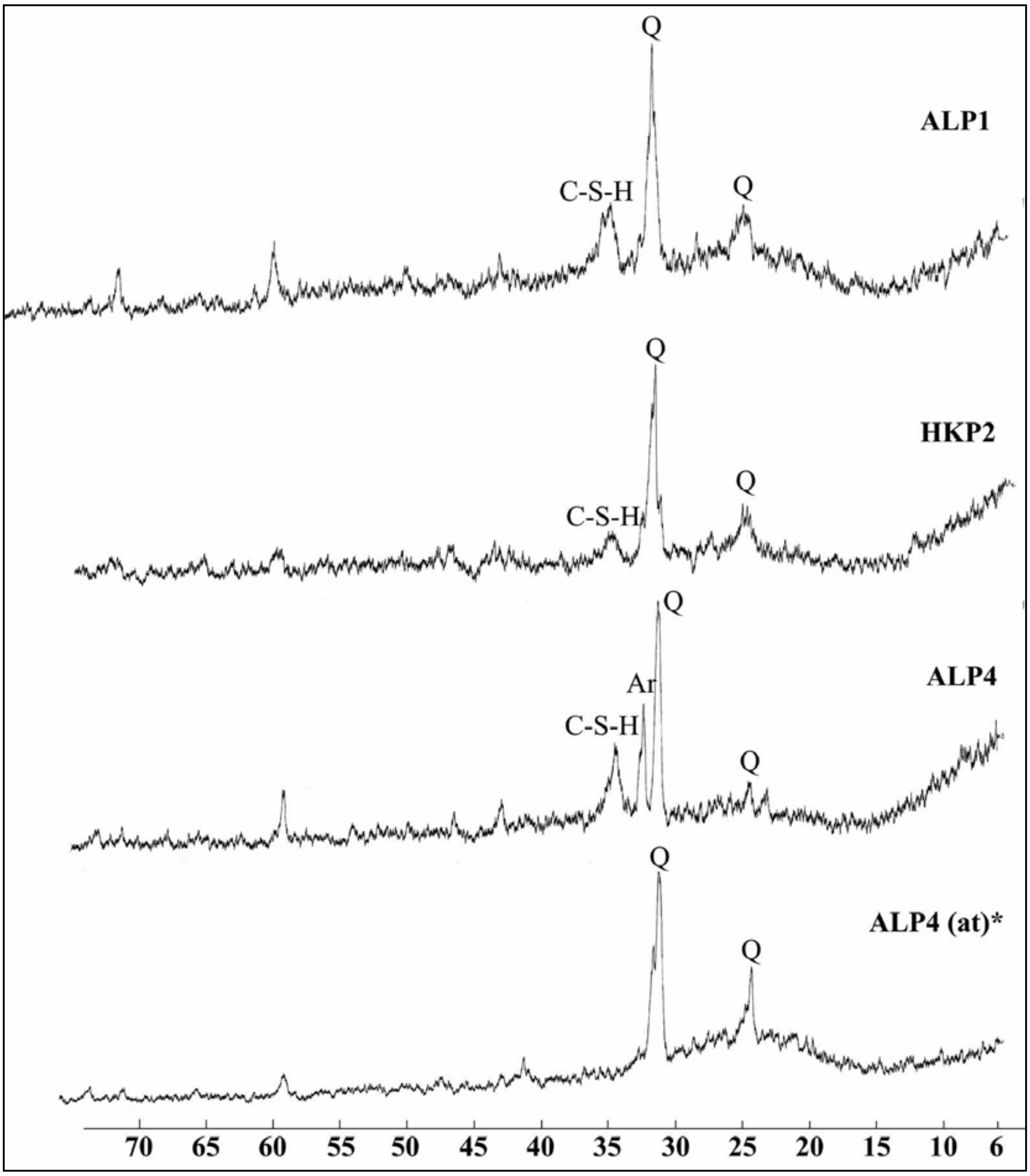


Fig. 3.23. XRD patterns of all red pigment layers and a white pigment layer of plasters. Notations are the same as given in Fig 3.20.
H: Haematite



2θ° Co K_α

Fig. 3.24. XRD patterns of finest aggregates (<125 μ) belonging to Alanya and Hasbahçe fine plaster layers after they are treated with saturated $Ca(OH)_2$ solution.
CSH: Tobermorite, Ar: Aragonite
* 5% HCl treated.

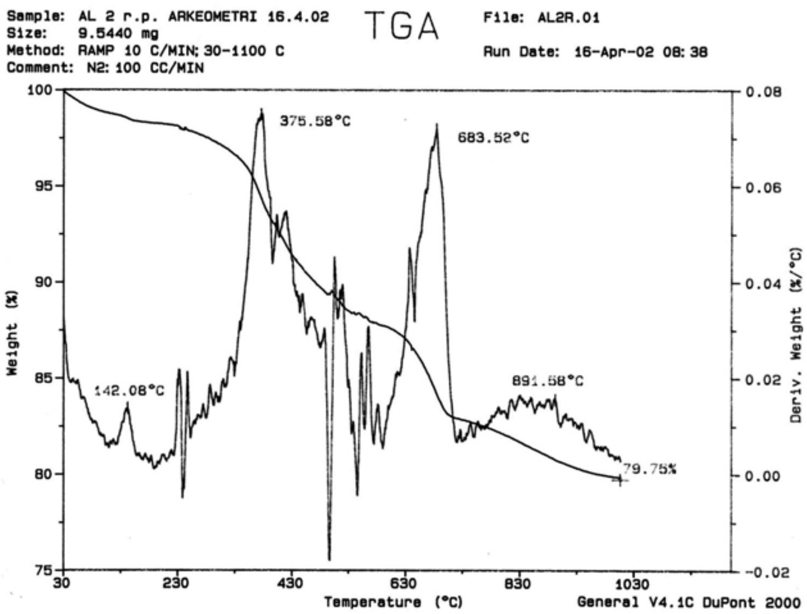
3.3.7.4 Termogravimetric Analysis

TGA traces of the fine plaster layers ALP2 and ALP4 showed that the calcite, the main mineral in its composition, was calcined at about 770^{0}C (Fig.3.25-26). It meant that the calcite was not the geological limestone which would be calcined at about 850^{0}C but the calcite formed through the carbonation of slaked lime (Bacolas et. al, 1995).

In one of the sample studied ,ALP4, organic matter was identified with a peak at 520^{0}C Its amount was estimated as about 5% (Fig.3.26).

TGA analysis of red pigment seemed to be somewhat complicated but the common feature of them was the presence of TGA peaks at about 140^{0}C and 375^{0}C which might be due to presence of opal-A. The physically held water in large capillaries of opal-A was lost below 150^{0}C (Jones and Segnit, 1969). Between 150^{0}C and 400^{0}C the weight loss was attributed to single OH's (silanols) bound to similar surfaces (Dixon and Weed, 1989, pp.939).

TGA trace of red pigment layer ALP2 rp showed additional peaks at about 683^0 C and 891^{0}C. The former was due to decomposition of carbonated slaked lime and the latter one was due to decomposition of micritic limestone aggregates (Fig.3.25).



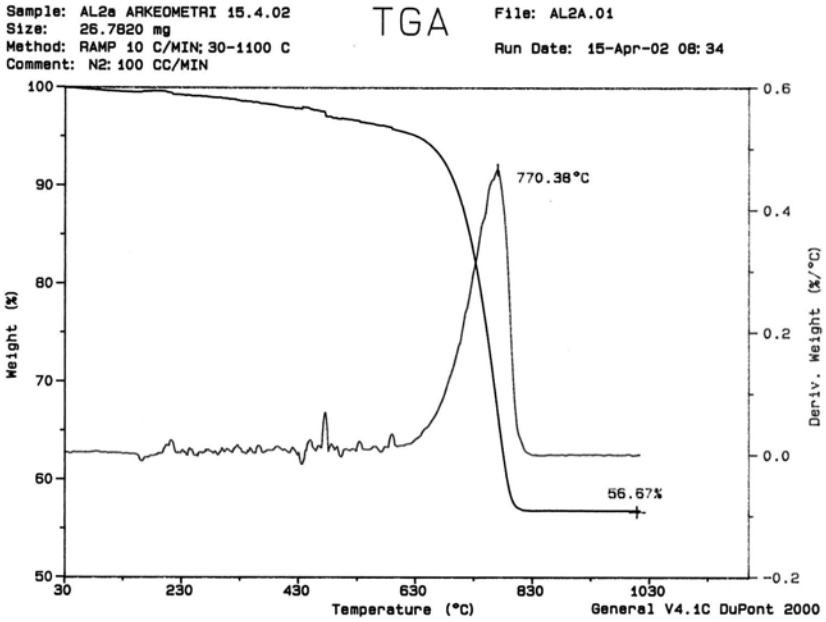


Fig. 3.25 TGA traces of a red pigment layer ALP2.rp and fine plaster layer ALP2.a

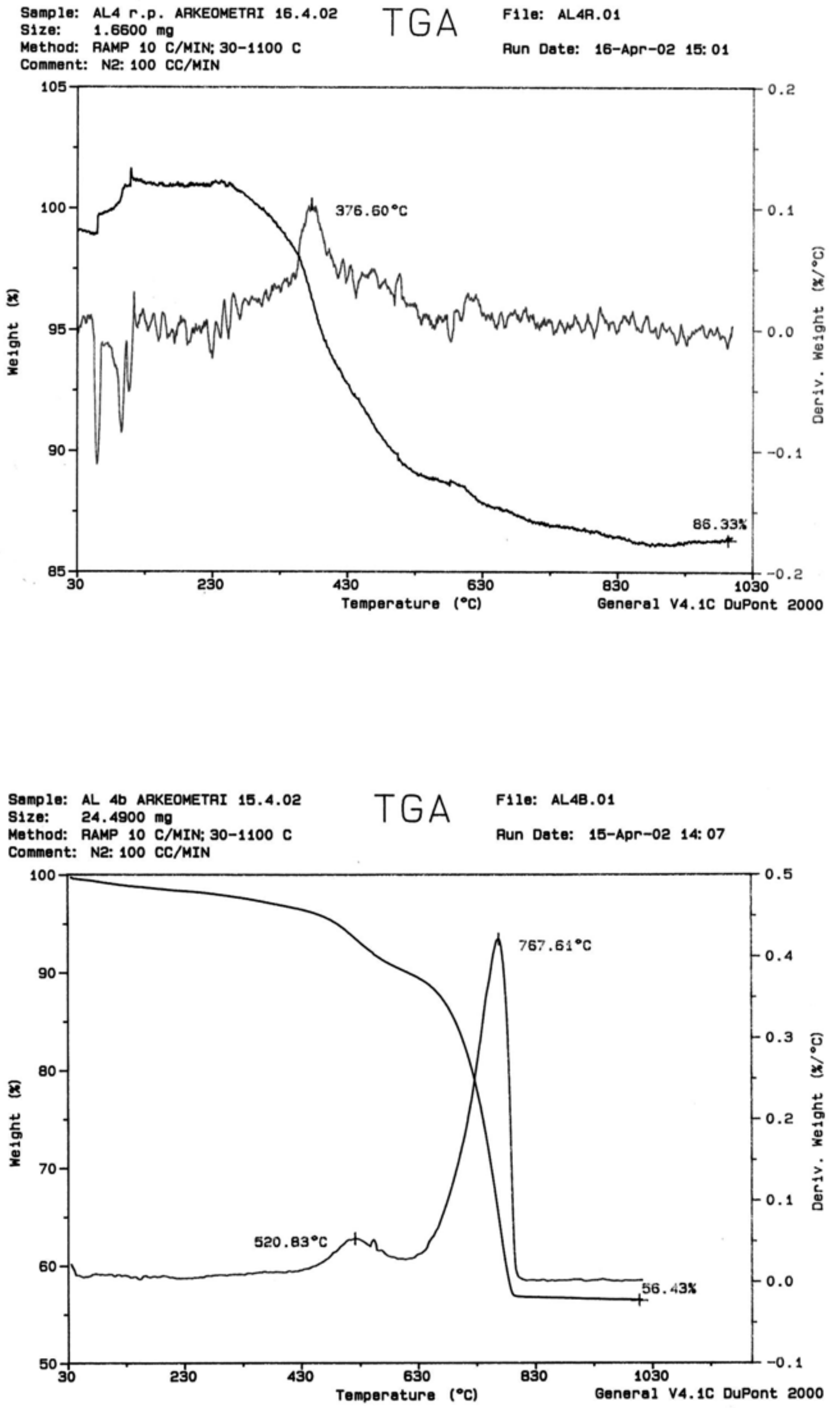
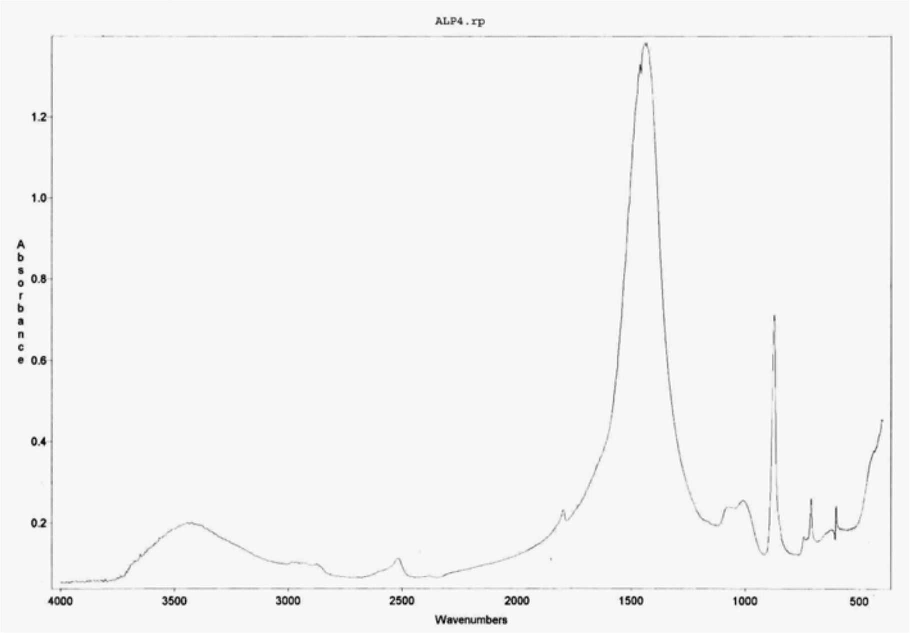


Fig. 3.26 TGA traces of a red pigment ALP4.rp and fine plaster layer ALP4.a

3.3.7.5 FTIR Analysis

FTIR spectra of red and green pigment layers of ALP4 and zigzag patterned red pigment ALP2 were taken. FTIR traces showed the presence of calcite with the stretching mode of carbonate at around
1450 cm^{-1} and its bending mode at around 875 cm^{-1} (Fig. 3.27). The broad peaks at around 1100 cm^{-1} and 800 cm^{-1} are due to the presence of opal-A and quartz. The broad peak at around 3500 cm^{-1} is due to the OH stretching mode of Opal-A (Fig. 3.27, 3.28). Colouring iron compounds could not be identified by FTIR. Red and green pigments show similar FTIR spectra.



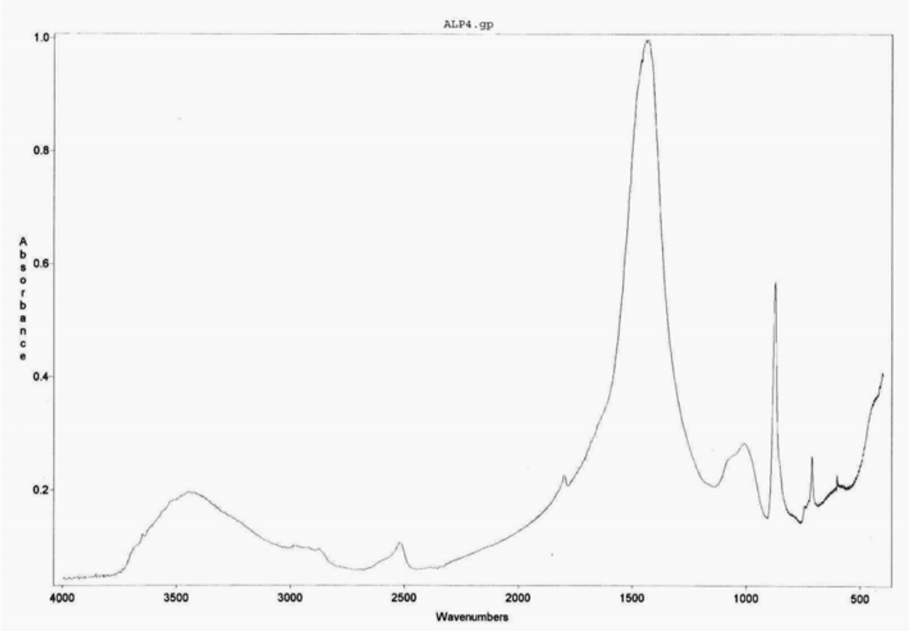


Fig. 3.27 FTIR traces of a red pigment layer ALP4.rp and a green layer ALP4.gp

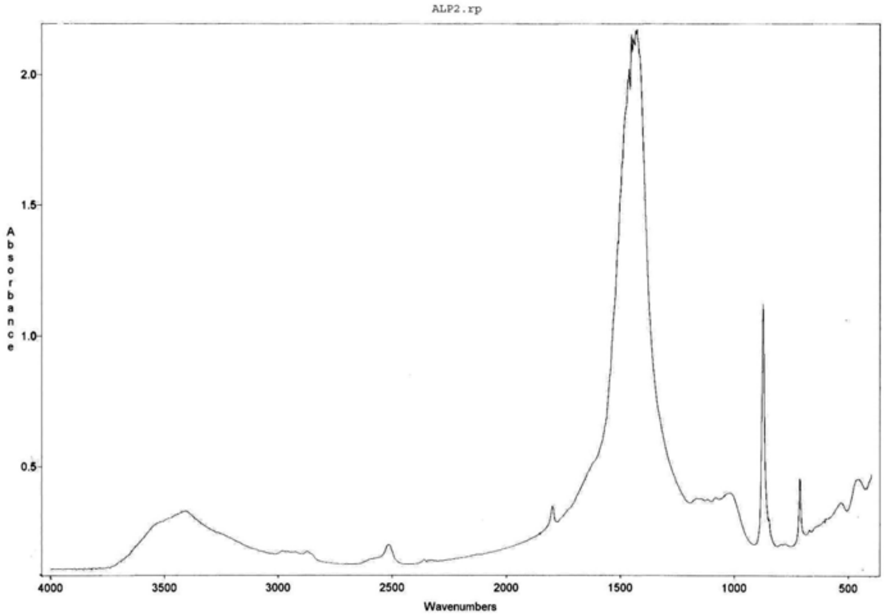


Fig. 3.28 FTIR traces of zigzag patterned red pigment layer ALP2.rp

3.4 Preparation of New Plasters and Their Ultrasonic Pulse Measurements

Two Kubadabad plaster aggregates of sizes <125 µ and 125µ were used for the preparation of new plasters as described in section 2.5. Some other plasters were prepared by using quartz aggregates.

Ultrasonic pulse velocities of plasters K1 and K2 with original aggregates were compared with those of Q1 and Q2 containing quartz aggregates. The results showed that original aggregates had lower velocity than those of quartz aggregates even if their bulk densities were almost equal. However, the bulk density values were not reliable for comparisons due to partial carbonation and high solubility of $Ca(OH)_2$. E_{mod} values were not reliable either (Table 3.5).

Table 3.5 Density, Ultrasonic Velocity and E_{mod} Values of New Plasters

Sample	**Density (g/cm^3)**	**Velocity (m/s)**	**Emod (Mpa)**
K1	0.71	587	225
Q1	0.82	790	471.32
K2	0.81	675	339
Q2	0.84	819	518.91

CHAPTER IV

DISCUSSION OF THE EXPERIMENTAL RESULTS

In this chapter, the experimental results that were obtained by the examination of the plasters from six monuments in Alanya, Antalya and Konya were interpreted in terms of physical and mechanical properties, raw materials composition and characteristics of binder, aggregates and pigments and durability properties of plasters.

4.1 Physical and Mechanical Properties of Plasters

4.1.1 Physical Properties

The basic physical properties obtained for the plasters (bulk density, porosity, water absorption capacity and water vapour permeability) showed that they are allowing easy passage to water vapour.

Majority of the plasters had the bulk density in the range of 1.30-1.50 gr/cm^3 and the porosity in the range of 30-49 % (Fig.3.1). It shows that those are low bulk density, high porosity building materials. The bulk density and porosity values were found to be comparable with those of lime plasters and mortars studied before such as an Ottoman building plasters in Bursa (Akyazı, 1998)

Water vapour permeability determinations showed that the μ values of the plasters ranged from 1.79 to 9.22 and the SD values ranged from 0.020m to 0.069m (Table. 3.1). These values are comparable with the values of mud plaster and lime plaster SD values of other studies such as mud and lime plaster layers of some traditional half timber houses in Ankara (Akkuzugil, 1997) and lime plasters of a Byzantine church (Nizamoğlu, 1998). It indicates good breathing property of the plasters. In other words, water vapour can travel easily through the plaster layers without the danger of condensation in the wall. This is an important specification of the plasters, which should be fulfilled and continued in the repair plasters.

4.1.2 Mechanical Properties

Mechanical properties of plasters were expressed by the modulus of elasticity, E_{mod} , values which were obtained indirectly from ultrasonic pulse velocity and the bulk density measurement using a mathematical equation (Section 2.3.1). Since the E_{mod} values obtained were not based on direct experimental measurements, they should be considered as approximate values.

For the majority of the samples, E_{mod} values were in the range of 1.50- 3.30 GPa (Fig.3.2). If the E_{mod} values of plasters were compared with those of the Seljuk mortars studied before (Tunçoku, 2000), it can be said that plasters fell almost in the same range with the Seljuk mortars. In addition, the E_{mod} values obtained were comparable with those of other historic building materials studied before (Moropoulou et al., 2000). A Byzantine Church in Kiev had E_{mod} of 1-3 Gpa for bricks and 0.6-0.7 GPa for mortar. Hagia Sofia in Istanbul had the E_{mod} of 3.1 for brick and 0.66 for mortar (Moropoulou et al., 2000).

The E_{mod} of plasters in this study show that they have enough mechanical strength comparable to some historic mortars and bricks. During the repair and restoration studies, the newly prepared materials should have the E_{mod} in the original plasters' range. It will be dangerous to have repair plasters of higher E_{mod} value in contact with the original plasters, since mechanical damage may occur in the original plasters during the induced stresses while the repair material may stay safe (Sasse and Snethlage, 1997; Fabbri and Grossi 2000).

Recent studies showed that E_{mod} value was an important parameter that affects normal cracking, deformation and scaling of the plaster layer independent of its thickness (Kevlar and Frosting 1998). The models developed through the experimental and mathematical relationships showed that lowering the E_{mod} of the plaster layer would decrease normal cracking and avoid scaling of the plaster layer. Experiments carried out on concrete wall which had an E_{mod} of 30GPa, would develop cracking with the plaster layer having an E_{mod} of 10Gpa, while no cracking with an E_{mod} of 5GPa. The research continues to clarify those relationships with the wall and the plaster (Kovler and Frostig 1998).

The historic plasters studied survived about 800 years on the walls. Therefore they must best define the ideal relationships of the wall and the plaster with respect to E_{mod} values to prevent normal cracking even if there were no other factors which would cause separation of the plaster layer from the wall. It can be concluded that the survival of the historic plaster layers depend on quite a number of properties they have in their technology.

4.2 Raw Material Composition of Plasters

It is obvious that the raw material properties of plasters define their final properties and their function on the masonry structures. Each component of the plasters; binder, aggregates, organic and/or inorganic additives, pigments, all take their own part within this context affecting the long term performance that is their durability. In the following subsections, experimental results will be interpreted in terms of the characteristics of those components of the plasters.

4.2.1 Characteristics of Binder Lime

Binder used in all plasters were found to be lime which was fully carbonated into micritic calcite. The plasters were with very high content of lime. The percentage of binder lime in almost all samples was found to be greater than 85%, about half of the fine plaster layers had about 95% binder lime. If compared with some Seljuk mortars, it was seen that they had about 60% lime on the average (Tunçoku, 2001). Although some limestone aggregates were clearly observed in thin section analysis which caused an increase in lime content, it is still possible to say that lime content of the plasters is very high.

TGA traces of the fine plaster layers showed that the calcite, the main mineral of the binder, was calcined at about 770^0C (Fig.3.25-26). It meant that the calcite was not the geological limestone which would be calcined at about 850^0C but the calcite formed through the carbonation of slaked lime (Bacolas et. al, 1995).

The binder lime was composed of very small crystals of calcite with the particle size < 4µ which was observed by the SEM images and by the optical microscopic analyses of thin sections. That indicates the use of very plastic fat lime with very fine particle size and very large surface area which would lead to an efficient carbonation process (see section 1.3). Hydraulic limes would not have such a high surface area (Table 1.1).

Combined analyses of optical microscopy, SEM-EDX, XRD, TGA revealed that micritic calcite crystals were together with very fine siliceous grains with the size less than 5µm. Those siliceous particles were identified as opal-A of very high pozzolanicity. Pozzolanic aggregates or additives were found to increase the carbonation process (see section 1.5). In addition, they had produced considerable amount of pozzolanic products in the binder matrix that will be discussed in more detail in the next subsection about aggregates. Very porous nature of the plasters is also an indication of an efficient carbonation process. One of the parameters affecting porosity and carbonation is the lime: water ratio and the relative humidity of the environment (Dheilly et al, 2002).

Possibility of an organic additive in the binder was proved with a peak at 520^0C in the TGA traces in some samples (Fig.3.26). Its amount was estimated as about 5%. Studies have shown that some organic materials might increase the crystallization of calcium carbonate (Young and Miller 2000, Güney, 2003).

4.2.2 Characteristics of the Aggregates

The aggregates will be described by their several characteristics.

The percentage and size distribution of aggregates: The percentage of aggregates were in the range of 3.15%-15% in fine plaster layers. Regarding to their particle size distribution it is possible to separate them into three groups; fine, coarse and mixed according to their average grain size. (Tucker, 1991) (see section 3.3.2).

Types of aggregates: The petrographic analysis of thin sections showed the presence of some aggregates in the matrix. They were identified as limestone aggregates (Fig 3.6b), some silicate minerals like muscovite (Fig. 3.7a,b), pyroxene (Fig. 3.8a,b), and phillite (Fig. 3.8a,b). In the red colored and red zigzag decorated plasters limestones of micritic calcite and opaque minerals were also identified in the pigment layers (Fig. 3.6a, 3.10b,c, 3.12a,b).

Pozzolanicity of the Aggregates: In this study, it was aimed to compare the pozzolanic activity of the plaster aggregates with those aggregates used in cement industry. The pozzolanic activity in the finest size of the aggregates (≤125μ), varied in the range of 4.20-42.00 mS/cm. It means that, all the plaster aggregates have very high pozzolanicity in comparison to the values of Luxan et. al, 1989. It is quite right to assume that the pozzolanic activity values of the aggregates in this study should be higher than the values given by Luxan et al, 1989, due to the longer reaction time that was ten days instead of two minutes of Luxan et al. It is known that the longer the time, the more possibility for the pozzolanic reactions to proceed on the available surfaces. In fact, some other researchers like Suzuki et al, 1985; Baronio and Binda 1997, suggested that pozzolanicity reactions should occur in a rather long time such as eight to ten days which was actually the time considered in this study.

Within the samples, the highest pozzolanic activity was observed in Alanya samples, the next ones being Syedra, Hasbahçe and Kubadabad samples respectively.

Pozzolanic Reaction Products on Fine Aggregates: The high pozzolanicity of aggregates would result in the formation of various C-S-H compounds in the fine and coarse plaster layers. Recrystallization experiments of section 2.4.4 showed that the main mineral product of pozzolanic reactions is tobermorite.

XRD traces of finest aggregates (<125μ) belonging to plasters ALP1, HKP2 and ALP4, which were treated with saturated $Ca(OH)_2$ solution, showed the presence of tobermorite as newly crystallized mineral (Fig. 3.24). Tobermorite was together with aragonite in one sample ALP4. After acid treatment, the peaks of tobermorite and aragonite disappeared as expected (Fig.3.24).

Formation of aragonite is an unexpected phenomenon. Its precipitation would be favored in a medium that had rather high pH like 13-13.5 (Kitamura et al, 2001). The pH of the saturated $Ca(OH)_2$ solution could be locally increased during the C-S-H formation process which could promote aragonite formation in preference to calcite.

An estimation of the amount of C-S-H in one of the fine plaster layers may be done as follows. Considering the amount of $Ca(OH)_2$ consumed by the fine aggregates that exist in about 2% in the fine plaster layers, and one mole of $Ca(OH)_2$ to give 1/5 mole of tobermorite with a possible formula of $5\ CaO.\ 6\ SiO_2.\ 2.5\ H_2O$, highest pozzolanic active sample ALP4 $\leq$ 125μ, would form about 3 gr Tobermorite per 100 g of sample. That means about 1.5 g of silica such as opal-A may convert into tobermorite and become soluble in acidic medium.

The estimated amount of 3% tobermorite in the fine plasters may indicate that pozzolanic reaction products should be important in the development of physical and mechanical properties of the plasters.

4.2.3 Characteristics of Pigments

Some of the plasters studied are decorated with red zigzag pattern on white coloured base. The pigment layer of plasters can be clearly distinguished from fine plaster layer due to size and porosity difference in thin section and SEM images. However, the pigment layer adhered well to the fine plaster layer proving that it was applied by using fresco technique. It meant that powdered pigment mixed with water was applied on the wet lime plaster (Fig.3.13a,b, 3.15a, 3.16a).

Haematite was found to be mineral of the red color. XRD analyses of these pigments layers, after treatment with 2% acetic acid, had shown the presence of haematite clearly, and the presence of opal-A and dolomite together with it (Fig.3.23). In the SEM-EDX analysis no other elements responsible for the red colour except iron was observed.

Characteristics of the haematite, can be described by its fine particle size in SEM images and the minerals which accompany it such as quartz, opal-A and dolomite. Their presence was proved by XRD, TGA and FTIR. Haematite peaks are not so sharp to indicate its well crystallized nature (Fig.3.23). The presence of opal-A as a broad peak in the same region, in XRD patterns prevents the observation of the complete peaks of haematite. Those minerals which accompany haematite such as opal-A and quartz with some dolomite were also indicated in FTIR traces of red pigments. They may indicate its source such as a haematite mineral rich in those minerals in nature. It is also probable that opal-A may be added to haematite pigment to increase the formation of pozzolanic reactions and durability of the pigment layer.

In the plaster ALP4, green color was detected under the red pigment layer. The XRD pattern of it indicated that, celadonite may be responsible for the color, which is a silicate mineral containing iron with lower oxidation number.

Red and green pigments show similar FTIR spectra.(Fig.3.27-28). Their EDX analyses are also the same. Pigments of iron compounds could not be identified by FTIR. Raman spectroscopy would clarify their identification.

The white pigment layer which formed the base of the red zigzag decorations was found to be calcite together with opal-A and quartz. In the SEM images, the calcite of the pigment layer was observed to be very fine particle sized and very well compacted (Fig. 3.13). White pigment calcite also contained opal-A and some dolomite to a total of about a few percent. The presence of opal-A both in red pigment haematite and white pigment calcite increases the possibility of its use as additive to promote pozzolanic reactions and increase durability of pigment layers.

4.3 Durability Properties of Plasters and Pigments

Durability properties of building materials have been usually expressed in numerical values using some physical and mechanical properties for stone, brick and mortar (Winkler 1989; Rodriguez and Jeremias,1990). Among these ,the ratio of uniaxial compressive strength in wet and dry states and the ratio of dry strength to porosity plus swelling strain were more commonly used (Winkler 1989; Rodriguez and Jeremias,1990). However, expressions of durability concerning plasters are rare. In this context, importance of E_{mod} values of plasters can be mentioned as it was discussed in section 4.1.2.

The physical properties of the plasters such as low bulk density, high porosity and good breathing property expressed as water vapour permeability and their relationship with the wall that carries the plasters should be the additional factors affecting durability.

On the other hand, well carbonated structure of binder lime and its micro texture, aggregate composition with highly pozzolanic components such as opal-A that had provided the formation of considerable amount of C-S-H in the matrix of the plasters and the pigment layers must have powerfully increased durability of plasters and pigments.

Durability of plasters may be also due to the presence of dolomite crystals that may affect carbonation in the positive way.

CHAPTER V

CONCLUSIONS

The principle conclusions of this research are given below.

- The plasters studied are low bulk density, high porosity building materials.

The μ and SD values of the plasters indicated that they have good breathing property. In other words, water vapour can travel easily through the plaster layers without the danger of condensation in the wall.

Those are important specifications of the plasters, which should be fulfilled and continued in the repair plasters.

- The E_{mod} of plasters in this study show that they have enough mechanical strength comparable to some historic mortars and bricks. During the repair and restoration studies, the newly prepared materials should have the E_{mod} in the original plasters range.
- Recent studies showed that E_{mod} value was an important parameter that affects normal cracking, deformation and scaling of the plaster layer independent of its thickness. However, those relationships with the wall and the plaster are complicated. The historic plasters studied survived about 800 years on the walls. Therefore they must best define the ideal relationships of the wall and the plaster with respect to E_{mod} values if more detailed investigations are done.
- Binder used in all plasters were found to be fat lime which was fully carbonated into micritic calcite. The percentage of binder lime in almost all samples was found to be greater than 85%, about half of the fine plaster layers

had about 95% binder lime. The micritic crystal structure of binder lime indicates the use of very plastic fat lime with very fine particle size and very large surface area which would lead to an efficient carbonation process. Hydraulic limes would not have such a high surface area.

- Micritic calcite crystals were together with very fine siliceous grains with the size less than 5µm. Those siliceous particles were identified as opal-A of very high pozzolanicity. They had produced considerable amount of pozzolanic products in the binder matrix. In addition, they must have taken important role in the carbonation process.
- The percentages of aggregates were in the range of 3.15%-15% including the pozzolanic aggregates in fine plaster layers. Regarding to their particle size distribution it is possible to separate them into three groups; fine, coarse and mixed according to their average grain size.
- Pozzolanic reaction products should be important in the development of physical and mechanical properties of the plasters.
- The plasters decorated with red zig-zag pattern on white coloured base were prepared by using fresco technique. It meant that powdered pigment mixed with water was applied on the wet lime plaster.
- Haematite was found to be mineral of the red color. Characteristics of the haematite can be described by its fine particle size and the minerals which accompany it such as quartz, opal-A and dolomite. Haematite peaks of XRD were not so sharp to indicate its well crystallized feature, accompanying minerals may indicate the source of haematite mineral in nature. It is also probable that opal-A may be added to haematite pigment to increase the formation of pozzolanic reactions and durability of the pigment layers.
- The white pigment layer which formed the base of the red zig-zag decorations was found to be calcite together with opal-A, quartz and dolomite. The presence of opal-A both in red pigment haematite and white pigment calcite increase the possibility of its use as additive to promote pozzolanic reactions and increase durability of pigment layers.
- Possibility of an organic additive in the binder was proved with a peak at 520^0C in the TGA traces.

- Well carbonated structure of binder lime and its micro texture, aggregate composition with highly pozzolanic components such as opal-A that had provided the formation of considerable amount of C-S-H in the matrix of the plasters and in the pigment layers must have powerfully increased durability of plasters and pigments. The physical properties of the plasters such as low bulk density, high porosity and good breathing property expressed as water vapour permeability and their relationship with the wall that carries the plasters should be the additional factors affecting durability.

Finally, it can be concluded that the survival of the historic plaster layers depends on quite a number of properties related to their technology. Further analyses will better define some points such as the type and the sources of opal-A, relationship of E_{mod} and other mechanical properties with the type of the walls, the origin of the pigments and identification of organic additives.

The studies on ancient plaster technologies are essential for their conservation and for the selection and preparation of repair plasters. The knowledge gained from them would help to improve modern plaster technology.

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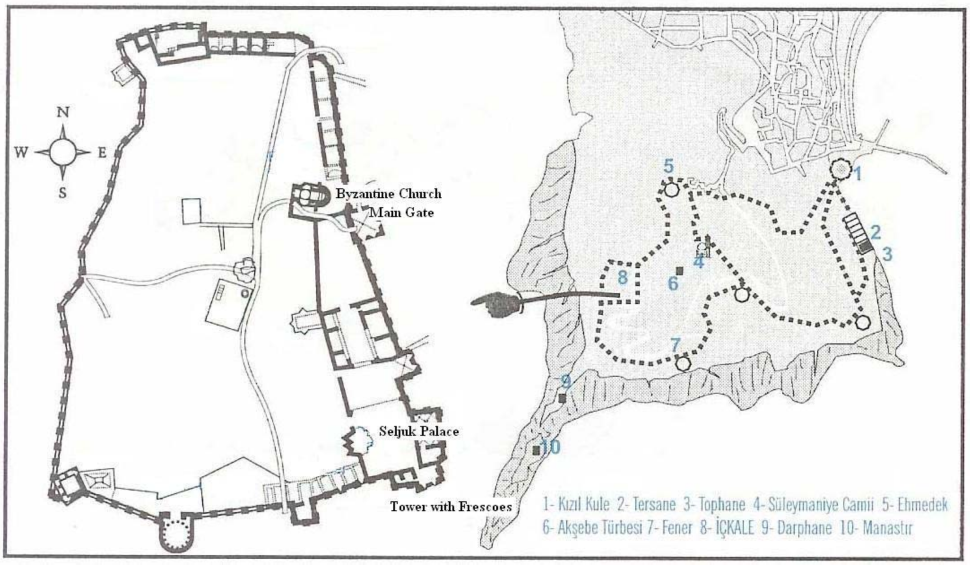
APPENDICES

APPENDIX 1

ALANYA CASTLE

1.a General View of Alanya Castle

1.b View of Zigzag Patterned Plaster (Cengiz Kabaoğlu, 2003; personal communication)

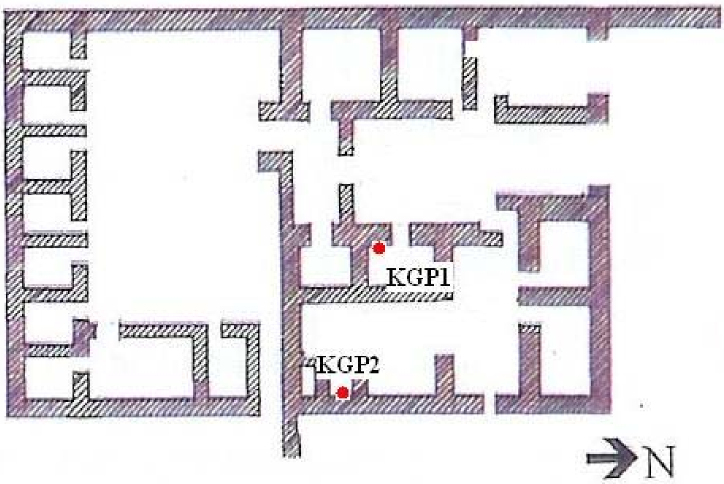


1.c Plan of Alanya Castle (Alanya Müze Müdürlüğü, 1998)

APPENDIX 2

KUBADABAD GREAT PALACE

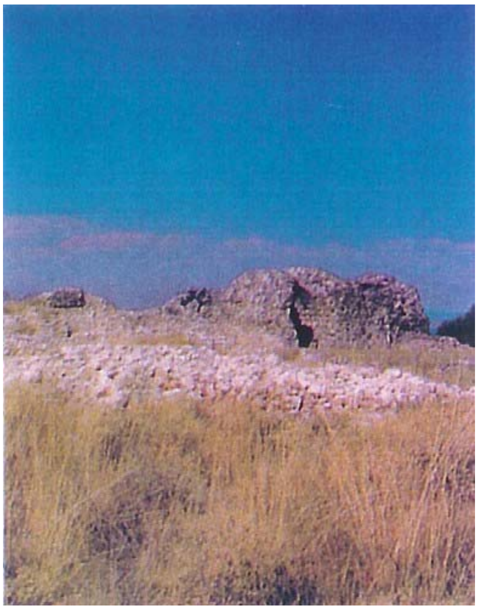
2.a General View of Kubadabad Great Palace



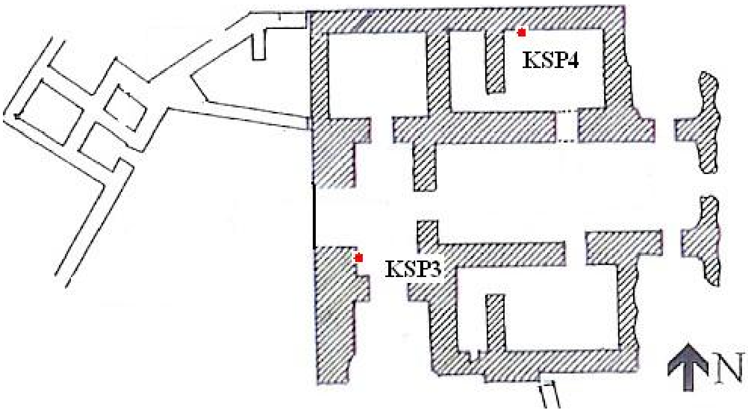
2.b Plan of Kubadabad Great Palace (Arık, 1968)

APPENDIX 3

KUBADABAD SMALL PALACE



3.a General View of Kubadabad Small Palace

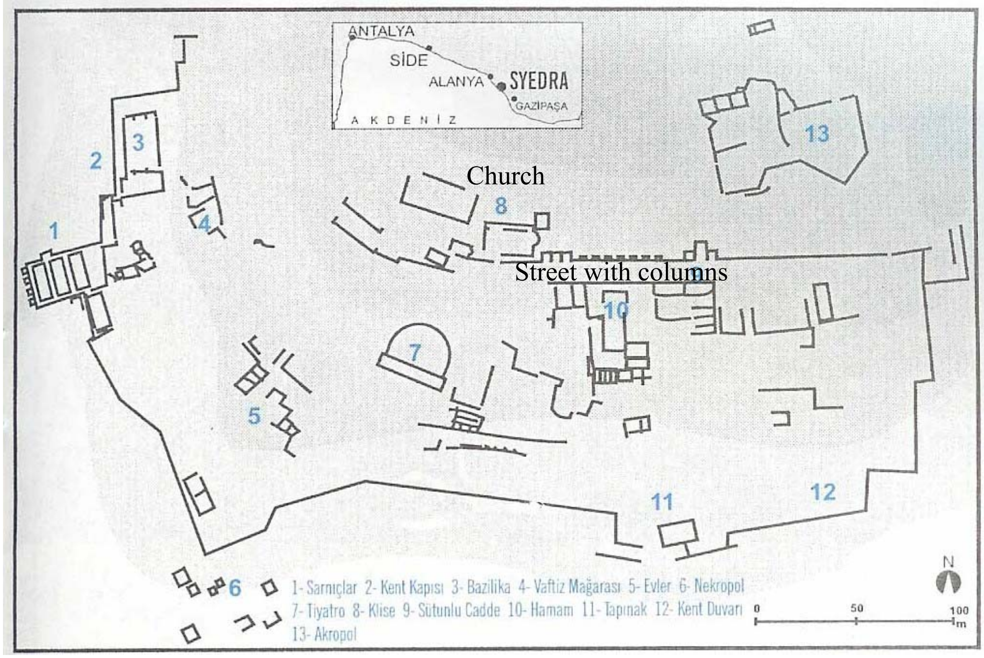


3.b Plan of Kubadabad Small Palace (Arık, 1968)

APPENDIX 4

SYEDRA ARCHAEOLOGICAL SITE

4.a General view of Syedra Archaeological Site
(Alanya Müze Müdürlüğü, 1998)



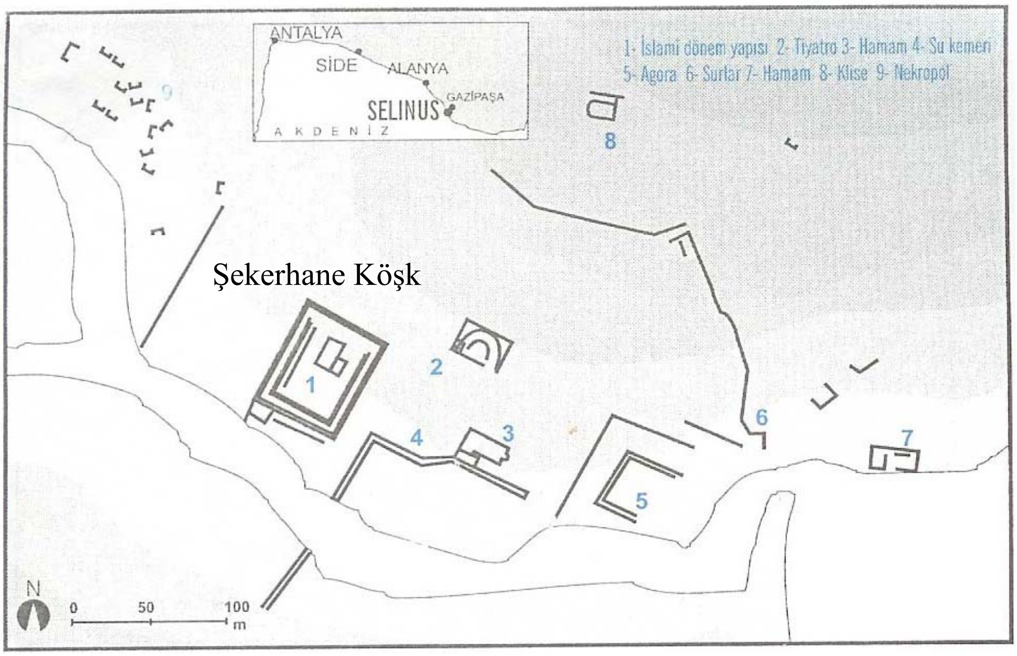
4.b Plan of Syedra Archaeological Site
(Alanya Müze Müdürlüğü, 1998)

APPENDIX 5

SELINUS ARCHAEOLOGICAL SITE

5.a General view of Şekerhane Köşk in Selinus Archaeological Site

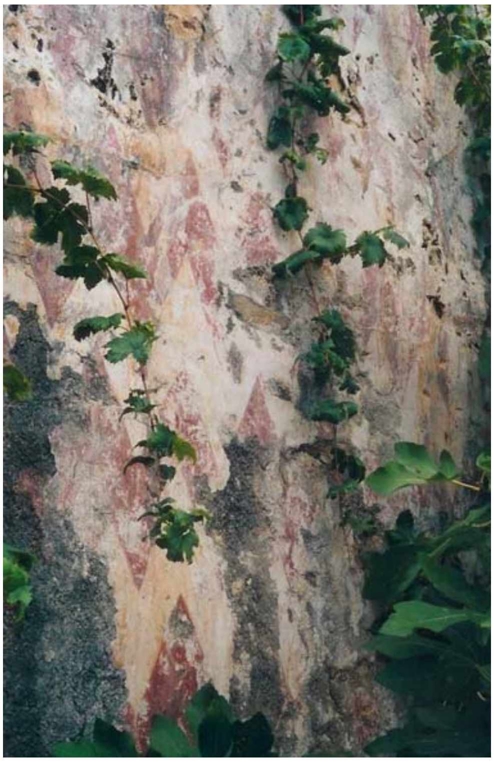
5.b View of zigzag patterned plaster on the interior wall of Şekerhane Köşk



5.c Plan of Selinus Archaeological Site
(Alanya Müze Müdürlüğü, 1998)

APPENDIX 6

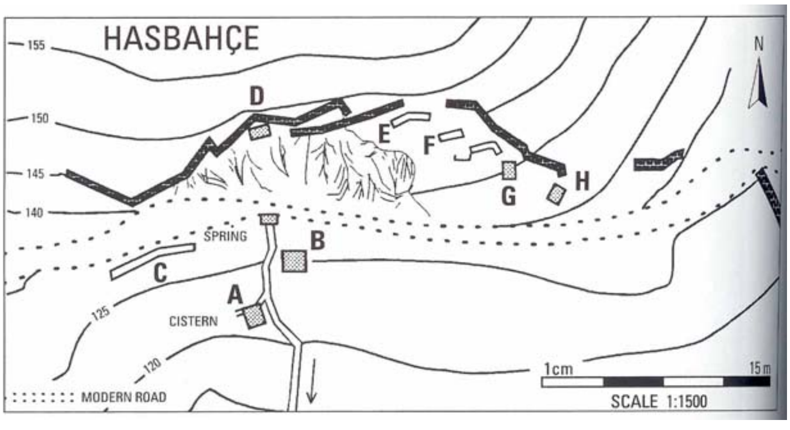
HASBAHÇE (ALANYA)



6.a View of zigzag patterned plaster on the exterior wall of building H

6.b View of zigzag patterned plaster on the exterior wall of building H

6.c View of zigzag patterned plaster on the exterior wall of building B



6.d Plan of Hasbahçe (Redfort, 2001)

APPENDIX 7

BASIC PHYSICAL PROPERTIES OF PLASTERS

Sample	**Mdry (g)**	**Msat (g)**	**March (g)**	**P (%)**	**D (g/cm3)**	**WAC (%)**
ALP1(1)	9.60	11.76	5.72	35.76	1.59	22.50
ALP1(2)	3.03	3.71	1.81	35.79	1.59	22.40
ALP1 (average)				**35.77**	**1.59**	**22.5**
ALP2(1)	2.29	3.14	1.32	46.70	1.26	37.10
ALP2(2)	1.85	2.44	1.10	44.03	1.38	31.80
ALP2 (average)				**45.36**	**1.32**	**34.5**
ALP3(1)	4,33	5,52	2,55	40.07	1.46	27.40
ALP3(2)	5.57	7.31	3.25	42.86	1.37	31.20
ALP3 (average)				**41.46**	**1.41**	**29.3**
ALP4(1)	2.19	2.85	1.30	42.58	1.41	30.10
ALP4(2)	2.30	2.99	1.41	43.67	1.46	30.00
ALP4 (average)				**43.12**	**1.43**	**30.1**
ALP5(1)	8.80	12.38	5.11	49.24	1.21	40.60
ALP5(2)	5.21	7.24	3.08	48.80	1.25	38.90
ALP5 (average)				**49.02**	**1.23**	**39.8**
ALP6(1)	6.46	8.49	3.87	43.94	1.40	31.40
ALP6(2)	10.31	13.66	6.13	44.49	1.37	32.40
ALP6 (average)				**44.21**	**1.38**	**31.9**
ALP7(1)	5.00	6.06	3.10	35.81	1.69	21.20
ALP7(2)	7.53	9.32	4.03	33.84	1.42	23.70
ALP7 (average)				**34.82**	**1.55**	**22.5**
ALP8(1)	1.14	1.37	0.69	33.82	1.68	20.10
ALP8(2)	3.45	4.12	2.00	31.60	1.63	19.40
ALP8 (average)				**32.71**	**1.65**	**19.8**
ALP9(1)	11.72	15.09	6.96	41.45	1.44	28.70
ALP9(2)	10.00	12.93	5.95	41.98	1.43	29.30
ALP9 (average)				**41.71**	**1.43**	**29.0**

KGP1(1)	4.90	6.46	2.78	42.39	1.33	31.80
KGP1(2)	3.49	4.72	1.98	44.89	1.27	35.20
KGP1 (average)				**43.64**	**1.30**	**33.5**
KGP2(1)	3.36	4.48	1.90	43.41	1.30	33.30
KGP2(2)	5.63	7.46	3.28	43.78	1.35	32.50
KGP2 (average)				**43.59**	**1.32**	**32.9**
KSP3(1)	3.57	4.31	2.08	33.18	1.60	20.70
KSP3(2)	4.12	4.91	2.39	31.35	1.63	19.10
KSP3 (average)				**32.26**	**1.61**	**19.9**
KSP4(1)	5.83	7.62	3.28	41.24	1.34	30.70
KSP4(2)	3.30	4.28	1.86	40.50	1.36	29.60
KSP4 (average)				**40.87**	**1.35**	**30.2**
SYDP1(1)	0.90	1.02	0.53	24.49	1.84	13.30
SYDP1(2)	0.84	1.00	0.50	32.00	1.68	19.00
SYDP1 (average)				**28.24**	**1.75**	**16.2**
SYDP2(1)	1.29	1.79	0.76	48.54	1.25	38.70
SYDP2(2)	1.30	1.81	0.78	49.51	1.26	39.20
SYDP2 (average)				**49.03**	**1.25**	**38.9**
SYDP3(1)	1.39	1.55	0.80	21.33	1.85	11.50
SYDP3(2)	1.54	1.72	0.92	22.50	1.93	11.60
SYDP3 (average)				**21.91**	**1.88**	**11.6**
SYDP4(1)	2.16	2.98	1.30	48.81	1.29	37.90
SYDP4(2)	3.58	4.83	2.16	46.82	1.34	34.90
SYDP4 (average)				**47.81**	**1.31**	**36.4**
SYDP5(1)	3.89	4.51	2.33	28.44	1.78	15.90
SYDP5(2)	3.92	4.55	2.40	29.30	1.82	16.00
SYDP5 (average)				**28.87**	**1.80**	**15.9**
SYDP6(1)	0.52	0.71	0.32	48.72	1.33	36.50
SYDP6(2)	0.88	1.12	0.50	38.71	1.42	27.20
SYDP6 (average)				**43.71**	**1.37**	**31.9**
ŞKP1(1)	6.46	7.08	3.71	18.40	1.92	9.50
ŞKP1(2)	3.17	3.52	1.85	20.96	1.90	11.00
ŞKP1 (average)				**19.67**	**1.90**	**10.3**
ASP1(1)	1.49	2.00	0.93	47.66	1.39	34.20
ASP1(2)	1.52	2.01	0.95	46.23	1.43	32.20
ASP1 (average)				**46.94**	**1.41**	**33.2**

HKP1(1)	6.26	8.42	3.76	46.35	1.34	34.50
HKP1(2)	1.74	1.90	1.00	17.78	1.93	9.10
HKP1 (average)				**32.06**	**1.63**	**21.8**
HKP2(1)	13.84	17.18	7.88	35.91	1.49	24.10
HKP2(2)	11.83	14.48	6.73	34.19	1.53	22.40
HKP2 (average)				**35.05**	**1.51**	**23.3**

APPENDIX 8

ULTRASONIC PULSE VELOCITY MEASUREMENTS AND MODULUS OF ELASTICITY OF PLASTERS

Sample	I (mm)	t (s)	V (m/s)	D (g/cm3)	Emod (MPa)
ALP1	15.2	14.4	1056	1.59	1632.95
ALP1	20.2	10.8	1870	1.59	5120.69
ALP1 (average)			**1463**	**1.59**	**3376.82**
ALP2	15.O	9.4	1596	1.26	2955.86
ALP2	15.1	9.8	1541	1.38	3018.09
ALP2 (average)			**1568.5**	**1.32**	**2986.97**
ALP3	11.3	12.8	883	1.46	1048.39
ALP3	11.2	6.6	1697	1.37	3633.56
ALP3 (average)			**1290**	**1.41**	**2340.97**
ALP4	4.9	8.3	590	1.41	452.03
ALP4	4.6	4.1	1122	1.46	1692.73
ALP4 (average)			**856**	**1.43**	**1072.38**
ALP5	17.2	10.4	1654	1.21	3048.63
ALP5	13.6	11.4	1193	1.25	1638.47
ALP5 (average)			**1423.5**	**1.23**	**2343.55**
ALP6	23.1	10.5	2200	1.40	6240.53
ALP6	22.9	12.5	1832	1.37	4234.67
ALP6 (average)			**2016**	**1.38**	**5237.60**
ALP7	13.5	15.4	877	1.69	1197.11
ALP7	14.6	9.3	1570	1.42	3223.56
ALP7 (average)			**1223.5**	**1.55**	**2210.33**
ALP8	14.2	8.2	1732	1.68	4641.44
ALP8	14.3	7.8	1833	1.63	5043.83
ALP8 (average)			**1782.5**	**1.65**	**4842.63**
ALP9	22.2	19.8	1121	1.44	1666.56
ALP9	16.4	10.6	1547	1.43	3151.84
ALP9 (average)			**1334**	**1.43**	**2409.20**

KGP1	14.3	12.7	1126	1.33	1553.02
KGP1	18.3	10.2	1794	1.27	3764.41
KGP1 (average)			**1460**	**1.30**	**2658.71**
KGP2	14.5	13.1	1107	1.30	1467.19
KGP2	14.5	13.1	1107	1.35	1523.62
KGP2 (average)			**1107**	**1.32**	**1495.40**
KSP3	14.4	14.1	1021	1.60	1536.10
KSP3	6.2	4.6	1348	1.63	2727.82
KSP3 (average)			**1184.5**	**1.61**	**2131.95**
KSP4	22.6	22.4	1009	1.34	1256.42
KSP4	14.1	12.9	1093	1.36	1496.33
KSP4 (average)			**1051**	**1.35**	**1376.37**
SYDP1	5.5	5.5	955	1.84	1545.51
SYDP1	5.9	4.4	1341	1.68	2782.37
SYDP1 (average)			**1148**	**1.75**	**2163.94**
SYDP2	8.1	6.9	1174	1.25	1586.70
SYDP2	10.2	7.4	1378	1.26	2203.52
SYDP2 (average)			**1276**	**1.25**	**1895.10**
SYDP3	12.6	9.2	1370	1.85	3197.87
SYDP3	10.8	7.5	1440	1.93	3685.79
SYDP3 (average)			**1405**	**1.88**	**3441.82**
SYDP4	8.5	6.4	1328	1.29	2095.24
SYDP4	7.7	5.7	1351	1.34	2252.49
SYDP4 (average)			**1339.5**	**1.31**	**2173.86**
SYDP5	16.1	9.9	1626	1.78	4334.20
SYDP5	10.7	5.3	2019	1.82	6832.70
SYDP5 (average)			**1822.5**	**1.80**	**5583.44**
SYDP6	4.8	3.5	1371	1.33	2302.37
SYDP6	6.9	4.7	1468	1.42	2818.31
SYDP6 (average)			**1419.5**	**1.37**	**2560.33**
ŞKP1	6.0	4.2	1429	1.92	3610.89
ŞKP1	8.7	5.1	1706	1.90	5092.84
ŞKP1 (average)			**1567.5**	**1.90**	**4351.86**

ASP1	13.2	8.5	1553	1.39	3087.49
ASP1	9.1	6.3	1444	1.43	2746.11
ASP1 (average)			**1498.5**	**1.41**	**2916.80**
HKP1	11.3	7.5	1507	1.34	2802.72
HKP1	4.5	3.3	1364	1.93	3307.00
HKP1 (average)			**1435.5**	**1.63**	**3054.85**
HKP2	15.0	12.3	1220	1.49	2042.46
HKP2	19.4	11.4	1702	1.53	4081.87
HKP2 (average)			**1461**	**1.51**	**3062.16**

APPENDIX 9

BINDER AND AGGREGATE PERCENTAGES OF PLASTERS

SAMPLE	%BINDER	%AGGREGATE
ALP1(1)	95.90	4.10
ALP1(2)	93.72	6.28
ALP1 (average)	**94.8**	**5.2**
ALP2(1)	94.23	5.77
ALP2(2)	95.73	4.27
ALP2 **(average)**	**94.9**	**5.1**
ALP3(1)	89.50	10.50
ALP3(2)	87.90	12.10
ALP3 (average)	**88.7**	**11.3**
ALP4(1)	95.80	4.20
ALP4(2)	93.85	6.15
ALP4 (average)	**94.8**	**5.2**
ALP5(1)	86.90	13.1
ALP5(2)	86.51	13.49
ALP5 **(average)**	**86.7**	**13.3**
ALP6(1)	95.36	4.64
ALP6(2)	93.90	6.1
(average)	**94.6**	**5.4**
ALP7(1)	95.07	4.93
ALP7(2)	94.91	5.09
ALP7 (average)	**95.0**	**5.0**
ALP8(1)	97.01	2.99
ALP8(2)	95.69	4.31
ALP8 (average)	**96.8**	**3.2**
ALP9(1)	92.90	7.10
ALP9(2)	90.64	9.36
ALP9 **(average)**	**91.7**	**8.3**

KGP1(1)	87.80	12.20
KGP1(2)	88.10	11.9
KGP1 (average)	**88.0**	**12.0**
KGP2(1)	76.28	23.72
KDP2(2)	76.86	23.14
KGP2 (average)	**76.5**	**23.5**
KSP4(1)	55.89	44.11
KSP4(2)	62.03	37.97
KSP4 (average)	**59.0**	**41.0**
SYDP1(1)	59.25	40.75
SYDP1(2)	61.47	38.53
SYDP1 **(average)**	**60.4**	**39.6**
SYDP2(1)	83.77	16.23
SYDP2(2)	87.67	12.33
SYDP2 **(average)**	**85.7**	**14.3**
SYDP3(1)	54.21	45.79
SYDP3(2)	53.39	46.61
SYDP3 (average)	**53.8**	**46.2**
SYDP4(1)	67.69	32.31
SYDP4(2)	69.65	30.35
SYDP4 (average)	**68.6**	**31.4**
SYDP5(1)	95.63	4.37
SYDP5(2)	96.87	3.13
SYDP5 (average)	**96.3**	**3.7**
ŞKP1(1)	85.01	14.99
ŞKP1(2)	87.53	12.47
ŞKP1 (average)	**86.3**	**13.7**
ASP1(1)	93.87	6.13
ASP1(2)	97.29	2.71
ASP1 (average)	**95.6**	**4.4**
HKP1(1)	90.70	9.30
HKP1(2)	89.19	10.81
HKP1 (average)	**90.0**	**10.0**
HKP2(1)	92.44	7.56
HKP2(2)	90.47	9.53
HKP2 (average)	**91.4**	**8.6**

APPENDIX 10

GRAIN SIZE DISTRIBUTION OF AGGREGATES

SAMPLE	**SIEVES**				
	% X>1000 µ	**% 500µ<X <1000µ**	**% 250µ<X <500µ**	**% 125µ<X <250µ**	**% X<125µ**
ALP1	10.2	16.9	18.7	28.8	25.4
ALP2	28.6	28.6	21.4	14.3	7.1
ALP3	14.6	17.1	17.1	26.8	24.4
ALP4	17.4	26.1	17.4	21.7	17.4
ALP5	11.7	16.0	23.4	28.7	20.2
ALP6	6.5	16.1	22.6	29	25.8
ALP7	56.6	15.1	9.4	11.3	7.6
ALP8	23.5	17.7	11.8	23.5	23.5
ALP9	5.3	9.3	21.3	37.4	26.7
KGP1	26.5	20.4	24.5	18.4	10.2
KGP2	13.8	24.8	39.4	14.7	7.3

KGP4	30.2	24.1	26.7	14.7	4.3
SYDP1	6	31	32.1	17.9	13.1
SYDP2	6.7	11.7	13.7	28.3	40
SYDP3	58.8	20.9	6.1	7.6	6.6
SYDP4	19.5	16.9	19.5	22.1	22
SYDP5	0	0	20	40	40
ŞKP1	25	15	20	20	20
HKP1	25	20.8	20.8	25	8.4
HKP2	25.6	19.5	20.7	23.2	11