DEVELOPMENT OF POZZOLANIC LIME MORTARS FOR THE REPAIR OF HISTORIC MASONRY

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ABSTRACT

DEVELOPMENT OF POZZOLANIC LIME MORTARS FOR THE REPAIR OF HISTORIC MASONRY

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The use of lime mortars with pozzolanic additives is of special importance for the repair of historic masonry. In this study, the effect of pozzolanic materials on the final characteristics of mortars was investigated. Metakaolin, fly ash and historic brick powder were used as pozzolanic materials in mortar mixes with varying binder:pozzolan:aggregate ratios. Historic mortar samples from rubble stone masonry of Kahta Castle, a medieval structure in close vicinity of the Nemrut Dağ Monument, were also investigated to serve as a starting point for the preparation of repair mortars. Physical and physicomechanical tests, optical microscopy, chemical tests, SEM-EDX and XRD analyses were used to assess the properties of the historic mortars and repair mortars.

Fat lime was found to be used in historic mortars with a high binder/aggregate ratio. They were observed to have relatively low density and high porosity with an average compressive strength of 7.4 MPa. Historic mortars were determined to have relatively high water vapour permeability and low water impermeability characteristics.

In repair mortars setting was found to be predominantly due to carbonation along with pozzolanic reactions. However, abundant presence of stratlingite in mortars with added metakaolin indicated that the pozzolanic reactions preceded carbonation in those mortars.

Use of pozzolanic materials increased the uniaxial compressive strength and modulus of elasticity of mortars compared with control samples. Using the same binder:pozzolan:aggregate ratio, highest increase was observed on mortars prepared with added fly ash at the end of 90 days. Durability parameters of repair mortars defined as wet to dry compressive strength were in the very good to excellent range according to Winkler's classification. By using fly ash, design of lime mortars with high water impermeability and high water vapour permeability characteristics was accomplished.

Keywords: repair mortars, historic masonry, pozzolan, carbonation

ÖZ

TARİHİ YAPILARIN ONARIMINDA KULLANILACAK PUZOLANİK KİREÇ HARÇLARININ GELİŞTİRİLMESİ

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Tarihi yapıların taş örgülerinin onarım çalışmalarında, puzolanik kireç harçlarının kullanımı önem taşımaktadır. Bu çalışmada, puzolanik katkı maddelerinin kireç harçlarının fiziksel, fizikomekanik ve mikroyapısal özelliklerine olan etkileri araştırılmıştır. Harç karışımlarında, puzolanik malzeme olarak metakolin, uçucu kül ve tarihi tuğla tozu, değişen bağlayıcı:puzolan:agrega oranları ile kullanılmıştır. Ayrıca, Nemrut Dağı Anıtı yakınlarında bulunan bir ortaçağ yapısı olan Kahta Kalesi'nin yığma duvarlarında kullanılan kireç harçlarının özellikleri onarım harçları hazırlanmasında bir örnek oluşturması amacıyla incelenmiştir. Hazırlanan onarım harçlarının ve tarihi harçların özellikleri, fiziksel ve fizikomekanik özelliklerin analizi, optik mikroskopla yapılan analizler, kimyasal analizler, SEM-EDX ve XRD analizleri ile belirlenmiştir.

Tarihi harçlarda saf kireçin kullanıldığı ve bağlayıcı:agrega oranlarının yüksek olduğu görülmüştür. İncelenen tarihi harçların, düşük birim hacim ağırlığı ve yüksek gözenekliliğe sahip olduğu ve ortalama basınç dayanımının 7.4 MPa olduğu tespit edilmiştir. Tarihi harçların su buharı geçirgenliğinin yüksek, su geçirimsizlik özelliklerinin ise düşük olduğu görülmüştür.

Onarım harçlarının katılaşmasının, karbonatlaşma ile birlikte puzolanik tepkimeler ile gerçekleştiği gözlenmiştir. Metakaolin kullanılarak hazırlanan harçlarda, yoğun olarak stratlingit oluşması, bu harçlarda puzolanik tepkimelerin öncelikli olduğunu göstermiştir.

Puzolanik katkı maddelerinin, harçların basınç dayanımı ve esneklik modülü değerlerini, kontrol örneklerine göre arttırdığı görülmüştür. Bağlayıcı:puzolan:agrega oranı sabit tutulduğunda, en yüksek artış, uçucu külün katkı maddesi olarak kullanıldığı harçlarda gözlenmiştir. 1:0.5:2 bağlayıcı:puzolan:agrega oranı kullanılarak hazırlanan haçların, ıslak basınç dayanımlarının, kuru basınç dayanımına oranı olarak tanımlanan, dayanıklılık parametrelerinin, Winkler sınıflandırmasına göre çok iyi ve mükemmel arasında olduğu tespit edilmiştir. Puzolanik katkı maddesi olarak uçucu kül kullanılarak, su geçirimsiz ve su buharı geçirimliliği yüksek kireç harçlarının oluşturulması başarılmıştır.

Anahtar kelimeler: onarım harçları, tarihi taş örgü, puzolan, karbonatlaşma

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CHAPTER 1

INTRODUCTION

Development and design of repair mortars compatible with the existing original materials of a historic structure requires several steps to be carried out; such as investigation of the structure, collecting original historical mortar samples, diagnostic analyses to determine the main causes of damage to the original materials to be repaired or replaced, investigation and characterization of the original mortar within its functional context, formulation of a repair mortar composition considering the above steps and testing the proposed repair mortar mixture for the required criteria (Schueremans 2011).

Repair mortars should be developed considering several aspects such as reversibility, compatibility, retreatability, durability, function and technology (Van Balen et al. 2000, 2005, Groot et al. 2005). Aesthetic properties of mortars should also be taken into consideration.

In the case of an intervention, the authenticity of a historical building should be taken into account and preserved as much as possible (ICOMOS 2003, 2005). Values embedded in a monument such as shape, design, materials and substance, use and function, tradition and techniques, workmanship, location and exposition have on their turn an artistic, historical, social and scientific dimension. Characterizing accurately all the values potentially embedded in a heritage structure requires significant effort in historical research, inspection and structural analysis (Schueremans 2011).

It is clear that mortars have an important function in the masonry and historic structure in general and thus have a great impact on the overall heritage values in most of the aspects and dimensions mentioned above.

During the intervention, including repairs with mortar, the minimum intervention principle applies (ICOMOS 2003, 2005) to ensure maximum preservation as possible. Compatibility is one of the most important aspects in the design of repair mortars such that it does not introduce any damage to the authentic materials. For repair mortars, the applied materials and techniques thus have to, under the given circumstances, fit with the original. Physical, mechanical and chemical compatibility between the repair and original mortar should be a priority (Faria 2008, Degryse et al. 2002, Mosquera et al. 2002).

In a structural context mortar is the material which holds the masonry units like stone and brick together as a bonding agent and thus enduring several structural inputs such as the gravity, movements due to soil settlements or seismic loads through its lifespan (Salvadori 1982; Holmes, Wingate 1997). Mortar between the masonry units also provide a cushion to spread the loads evenly particularly with soft bricks and stones distributing stress to the entire masonry. Furthermore, it also acts as a wick to draw moisture out of a wall providing the surface for evaporation (Holmes, Wingate 1997).

Since mortar is exposed to the effects of atmospheric conditions like wetting-drying, freezing-thawing cycles related with the ambient relative humidity and temperature with the rest of the structure, the characteristics of the mortar are directly related with the long term durability of the masonry (Schaffer 1972).

Studies with historic masonry show that the mortar within a masonry exhibit similar physical and mechanical properties with the materials they were used with, making the masonry a homogeneous unit behaving uniformly against the physical and environmental stresses (Tuncoku 2001, Biscontin et al. 1993, Livingston 1993). It was found that the mortar used with bricks for the construction of historic upper structures were to be prepared with aggregates with lower density and higher percentages of lime to match the physical and mechanical properties of bricks units (Tuncoku 2001; Livingston 1993). But for the stone masonry in the same historic structures, mortars with higher density and compressive strength were utilized (Tuncoku 2001, Biscontin et al. 1993).

The characteristics of the mortar used within a structure differ depending on the properties required by their function in the building and the conditions in which the mortar performs its duty. If for example when water insulation was needed or the structure was constructed in an environment where water was in constant contact with the materials, mortars having water impermeable character and the ability to set under water were used (Genestar et al. 2006; Ashurst, Dimes 1990; Malinowski 1981).

It is important to have detailed knowledge about the physical and mechanical properties, the raw material and compositional characteristics of historic mortars in order to understand the technology behind their use and utilize that information for the production of compatible and durable repair mortars.

Mortar consists of a binder and aggregates. Binder can be lime, mud, gypsum or cement. Aggregates are used as filler and to avoid cracking during the drying and setting of the binder (Mora et al. 1984; Arshust, Dimes 1990). Natural sand, gravel, crushed stones and brick, tile dust can be used as aggregates. Both the characteristics of the lime used and the properties of aggregates play important roles on the final characteristics of the mortar (Sanchez-Moral et al. 2005; Moropoulou et al. 1999, 2005a; Papayianni, Stefanidou 2005, Genestar et al. 2006, Lanas et al. 2004).

Characterization of historic mortars was primarily based on traditional wet chemical analyses until 1980's (Jedrzejewska 1960, Frizot 1981, Cliver 1972).

But without a solid knowledge of the nature of the mortar components it is often difficult or impossible to interpret the results. Mortar characterization and identification studies later on focused on the optical microscopy and X-ray diffraction analyses as the initial step for the qualitative identification of mortar components. Afterwards the use of several analytical techniques like SEM-EDX, DTA/TGA, FTIR etc. to quantitatively and qualitatively determine the components of the mortar became quite common (Middendorf et al. 2000; Van Balen et al. 2000; Martinet et al. 2000; Van Balen et al. 2003). For the field of conservation, characterization of historic mortars in relation to their raw material components is essential to formulate compositions for compatible repair mortars (Elert et al. 2002; Henriques 2004; Papayianni 2005). For the design of compatible repair mortars the most critical information to be gathered are the type and hydraulicity of the binder, the aggregate binder ratio and the characteristic properties of the aggregates like particle size distribution and pozzolanic activity (Leslie, Gibbons 2000). To ensure a durable connection between the original materials and the repair mortar, the mechanical and physical properties of the mortar must be adapted to that of the original (Sasse, Snethlage 1997). Therefore it is very important to analyze the physical and mechanical properties, compatibility and durability properties of the repair mortars in relation to the original mortars and to have detailed information about the factors affecting the final properties of the mortars with regard to the materials used and their compositional proportion.

Although there are several studies analyzing the physical and mechanical properties of the historic mortars; finding out the nature of the original raw materials, composite compositions and the techniques that were used to prepare mortars with the characteristics in question is a difficult task (Genestar et al. 2006; Elsen 2006). The main difficulty for the characterization of the historic mortars is to differentiate the nature of the binder in terms of hydraulicity, because of the similarities of the end products of pozzolanic reactions and hydration products of hydraulic components. Although determination of high amounts of calcium carbonate in historic mortars (Moropoulou 2005a; Genestar 2006; Tuncoku 2001, Moropoulou 2000) is an indication of the use of fat lime, the question on the origin of siliceous cementious end products is still open to investigation.

1.1 Lime mortar

According to the setting behaviour which is related with the type of lime and aggregate used, lime mortars can be classified as non-hydraulic and hydraulic lime mortars (Lea 1970, Moropoulou 1999, 2005a, 2005b). In non-hydraulic lime mortars pure lime is used as the binder. Non-hydraulic lime mortars have a long setting time requiring carbon dioxide from the atmosphere for the carbonation process to occur. Hydraulic lime mortars, setting is the result of hydration of the cementious components and/or pozzolanic reactions accompanied by the carbonation of the lime. Their setting time is shorter compared with non hydraulic pure lime mortars (Moropoulou 2005a). Hydraulic lime mortars can be further grouped as natural hydraulic lime mortars and pozzolanic lime mortars (Moropoulou 2005b). Natural hydraulic lime is used as the binder in natural hydraulic lime mortars.

Hydraulicity in pozzolanic lime mortars is achieved with the use of pozzolanic aggregates or additives used with lime. In this case the setting is the result of pozzolanic reactions that take place between lime and the pozzolans. Carbonation of calcium hydroxide also takes place simultaneously in pozzolanic lime mortars. Lime used can be either fat lime or natural hydraulic lime.

Hydraulic lime mortars are known with their higher mechanical properties compared with that of pure lime mortars (Lanas et al. 2004; Moropoulou 2005b; Teutonico 1994 mortars, generally decreasing the early strength and increasing water vapour permeability (Teutonico et al. 1994). Pure lime mortars have considerable higher water vapour permeability but lower early mechanical strength (Teutonico et al. 1994), but improvement). As the hydraulicity increases water vapour permeability of the mortars decreases (Banfill, Foster 2004, Teutonico et al. 1994). Gauging natural hydraulic lime mortars with pure lime alters the mechanical properties of the on the mechanical properties is observed for prolonged curing times (Lanas, Alvarez 2003). Also more binder content to a certain limit has an increasing effect on the mechanical strength for pure lime mortars due to the formation of higher values of open porosity which allows better carbonation (Lanas et al. 2006). But a decrease in porosity in pure lime mortars is observed in time due the evolution of carbonation (Papayianni, Stefanidou 2006). Also the water/lime content affects the porosity formation in lime mortars and increases with increasing water content (Papayianni, Stefanidou 2006). The hydraulicity, physical and mechanical properties of the mortars can be altered with the addition of pozzolanic additives. This is a very advantageous aspect of pozzolanic lime mortars, since its properties can be manipulated by adjusting the amount of pozzolanic additive used in the mortar mixtures. Increasing the amount of pozzolans to the mortar mixture generally enhances the mechanical strength of the mortar (Banfill, Foster 2004, Teutonico et al. 1994, Cerny et al. 2006). Use of pozzolans also improves the thermal properties of the mortar and decrease the water vapour permeability (Cerny et al. 2006). Pozzolanic additives also affect porosity in lime mortars decreasing porosity and increasing density. (Moropoulou et al. 2005b). The effects of the pozzolanic materials on mortar properties vary with the nature of the pozzolan (Agarwal 2006, Moropoulou et al. 2005a, Cerny 2006). Pozzolanic activity of a pozzolan which will be explained in detail is good indicator of the potential of the pozzolanic materials.

1.1.1 Lime, the binder

The raw material for the production of lime is *limestone* which is primarily composed of the mineral calcite, (calcium carbonate, $CaCO_3$). Limestone is rarely found as pure calcite in nature. Impurities like magnesia (MgO), silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3) in the form of complex silicates like clay can be present in limestone. If the percentage of these impurities is less than 5%, limestone is classified as high-calcium limestone.

1.1.1.2 Fat lime (high calcium lime)

Fat lime is produced by burning high calcium limestone in a kiln at a temperature of 900 °C. This process is called *calcination*. During the calcination process calcium carbonate ($CaCO_3$) gives off carbon dioxide (CO_2) and converts to calcium oxide (CaO) which is called *quicklime* (Davey 1961; Boynton 1966).

$$\underset{\text{limestone}}{CaCO_3} \xrightarrow{900\ °C} \underset{\text{quicklime}}{CaO} + CO_2$$

To obtain the *lime putty* which is the form used as binder in the preparation of mortar, quicklime is treated with water. When in contact with water, calcium oxide reacts with water with an exothermic process to form calcium hydroxide ($Ca(OH)_2$). The end product is called *slaked lime* and this process is called *slaking*.

$$\underset{\text{quicklime}}{CaO + H_2O} \longrightarrow \underset{\text{slaked lime}}{Ca(OH)_2} + \Delta H \text{ (heat release)}$$

If calcium oxide is hydrated with a precisely controlled stoichiometric amount of water then the product is a dry powder of calcium hydroxide which is termed as *dry hydrate of lime*. Fat lime produced by high calcium limestone is also commonly called high calcium lime or pure lime. Fat lime must be in contact with atmospheric carbon dioxide for the process of carbonation to take place, thus it can not set under water. Because of this requirement, pure lime is sometimes referred to as *air lime*.

1.1.1.3 Hydraulic lime

Hydraulic lime which can set under water without the need of carbon dioxide is produced with the same procedure as the high calcium lime; by calcination at temperatures between 900-1250 °C, but using siliceous or argillaceous limestones containing varying amounts of silica, alumina and iron. The temperature must be closely controlled and is usually higher than in ordinary lime kilns to ensure that much of the impurities combine chemically with lime without sintering calcium oxide (Boynton 1966). After calcination the end product is hydrated with sufficient water to convert free CaO into $Ca(OH)_2$, without hydrating the cementious components (Oates, 1998). If the free calcium oxide content is between 10 to 15%, the hard sintered lumps disintegrate into a powder. Otherwise, the lime must be ground before hydration (Boynton 1966). Final product after slaking contains various amounts of quicklime (left unslaked after slaking), hydrated lime, dicalcium silicate, calcium aluminate, calcium carbonate (left unchanged after calcination or carbonated from calcium hydroxide), tricalcium silicate and monocalcium silicate in approximate order of decreasing concentration (EN 459-1). The hydraulic properties of these limes come from the reaction products; calcium silicates and calcium aluminates formed during the calcination process and setting is the result of hydration of these products accompanied by the carbonation of the free lime.

According to their degree of hydraulicity, these limes are traditionally classified as i. feebly hydraulic lime, ii. moderately hydraulic lime, iii. eminently hydraulic lime. Hydraulic limes are also classified by a criteria called cementation index (CI), based on the analyses of lime. Cementation Index is calculated by the following equation:

$$\mathrm{CI} = \frac{(2.8 \times \%\,\mathrm{SiO_2}) + (1.1 \times \%\,\mathrm{Al_2O_3}) + (0.7 \times \%\,\mathrm{Fe_2O_3})}{\%\,\mathrm{CaO} + (1.4 \times \%\,\mathrm{MgO})}$$

In the equation higher weighting to is given the silica content, as lime-silica ratio is the controlling factor for the hydraulicity (Boynton 1966).

EN 459-1 classifies natural hydraulic limes in three strength categories as 2, 3.5 and 5 according to their minimum compressive strengths after 28 days. The general properties of hydraulic limes are summarized in table 1.

Table 1. Characteristics of hydraulic limes (Boynton 1966, EN 459-1)

	Type of hydraulic lime		
Parameter	2	3.5	5
	Feebly	Moderately	Eminently
Compressive strength (N/mm^2)	2-7	3.5-10	5-15
Active clay minerals (%)	<12	12-18	18-25
Cementation index	0.3-0.5	0.5-0.7	0.7-1.1
Setting time in water (days)	<20	15-20	2-4
Slaking time	slow	slow	very slow

1.1.2 Aggregates

Aggregates are important components of mortar systems. One of the functions of the aggregates is to inhibit shrinkage on drying and prevent cracking (Davey 1961; Mora et al. 1984; Arthurst, Dimes 1990). They also act as fillers in the mortar. Aggregates also contribute to the volume stability, durability and structural performance of the mortar system (Taylor 1997, Mehta 1986). They can be from various types of geological deposits including several types of sand resources, crushed rock formations. Apart from their mineralogical composition, their volume, content in the mixture, maximum size and size graduation influence the structure of the mortar (Neville 1995, Taylor 1997). Performance characteristics of mortars were found to be closely related to the binder/aggregate ratio and characteristics of aggregates such as the type, grain size distribution and shape (Papayianni et al. 2006, Stefanidou et al. 2005, Lanas et al. 2003). Grain size distribution of the aggregates affected the physical and physicomechanical properties of mortars. Fine aggregates (<2mm) contributed to higher strength in mortars in comparison to the ones having coarser aggregates such as medium sized pebbles up to 16 mm (Lanas et al. 2003; Stefanidou, Papayianni 2005). Coarse aggregates were found to be advantageous for the long term strength and for the prevention of cracks (Stefaniodu, Papayianni 2005). Use of rounded shaped aggregates could lead to the formation of larger pores due to the weaker cohesion between the binder and the aggregate. On the other hand angle-shaped aggregates caused a better packed structure and a decrease in larger pores thus an increase in mechanical strength (Lanas et al. 2004).

Lime mortars prepared by using limestone aggregates showed higher strengths because of the compatible nature of the binder and the aggregate (Lanas et al. 2004, Lanas, Alvarez 2003). Use of silicate aggregates with lower amounts of very small particles sizes led to better carbonation (Lawrence et al. 2006). If the aggregates used in mortars were inert they did not react with the binder but only function as the filler. But if they were active and reacted with lime they gave the mortar hydraulic properties (Arhurst, Dimes 1990). Siliceous fine aggregates of pozzolanic character with diameters <125μm were found to improve the mortars' strength and gave waterproofing character to mortars (Lanas et al. 2003, Degryse et al. 2002).

1.1.3 Pozzolanic aggregates or additives

A pozzolanic material is described as “a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties” (ASTM C618). As the definition implies pozzolanic materials react with lime in the presence of controlled amounts of water and produce a solid mass bound by calcium silicates and aluminates. The name pozzolan comes from Pozzouli, a city near Naples, Italy since Romans first used volcanic ash from that region to make a blend with slaked lime for the production of Roman Cement. Unlike natural hydraulic limes that are produced by calcining limestone with clay impurities, lime pozzolan mixtures are made solely by combining and milling lime with pozzolanic material (Boynton 1966). Lime pozzolan mixtures also show hydraulic properties, the setting action of natural hydraulic lime with regard to the formed end product, calcium silicate hydrates.

Almost all historic lime mortars were found to have pozzolanic characteristics either due to the use of natural or artificial pozzolanic fine aggregates most probably used as additives. Those pozzolanic additives contributed to the strength of mortars through pozzolanic reactions (Papayianni, Stefanidou 1997, Moropoulou et al. 2000, Tuncoku et al. 2006, Budak et al. 2010, Schueremans et al. 2011).

Pozzolans can be either of natural origin or artificially prepared;

Natural pozzolans: Pozzolans of volcanic origin are glassy materials or compacted tuffs originated from the deposition of volcanic dust and ash which have undergone rapid cooling and subjected to some chemical alterations leading to the formation of zeolitic compounds (Lea, 1970). Diatomaceous earths and siliceous rocks of biogenic origin and silica rich substances of inorganic origin such as cherts, flints, shales and sandstones are also pozzolans that can be grouped under pozzolans of natural origin (Lea 1970; Diamond 1976).

Artificial pozzolans: These pozzolans are produced by burning clay or shales to dehydroxilate and activate the material. Raw clays consist primarily of a group of hydrated aluminium silicates. These clays contain considerable amount of water. Some of the clays like kaolinite types, loose the combined water at 500 ºC while some such as montmorillonite at relatively lower temperatures (Lea 1970).

Pozzolanic materials influence the final characteristics of lime mortars to a great extent (Moropoulou et al. 2005b, Chakchouk et al. 2006, Cerny et al. 2006). This affection is both due to the formation of CSH networks throughout the binder matrix and the interface between the binder and the pozzolanic aggregates. The reaction between the coarse aggregates showing pozzolanic properties and calcium hydroxide leads to a strong attachment between the aggregates and the binder at a molecular level such as in mortars with brick aggregates. In the case of non-pozzolanic aggregates the interlocking of the aggregate-binder paste forms the transition zone which is characterized as the weak phase because of the formation of the micro cracks and different crystal sizes of the binder (Tasong et al. 1998, Lea 1970). The incompatibility between the modulus of elasticity of the aggregate and the binder also affect the development of these micro cracks at the aggregate-binder interface. But the use of pozzolanic aggregates enforces the adherence of the binder to the aggregates leading to a more durable mortar system. The use of pozzolanic materials in powder form improves the performance of the mortar (Moropoulou et al. 2005b, Cerny 2006) by enhancing the mechanical and physical properties of the binder matrix and helping the adjustment of the mechanical and physical properties of the binder matrix to match that of the aggregate by the result of pozzolanic reactions. If pozzolanic additives are highly active and used extensively in lime, most of the lime reacts with the pozzolan during pozzolanic reactions surpassing carbonation (Velosa, Veiga 2004). The results of the study of Velosa and Veiga shows that when metakaolin is used in a 1/1 (m/m) ratio with lime, DTA/TG analyses shows small amounts of $CaCO_3$ after 28 days which may lead to the fact that pozzolanic reactions are favoured to carbonation if pozzolans with high activity are available at all times. The performance enhancing effect of the pozzolans varies with their characteristics. When used with lime for the preparation of mortars, pozzolanic materials can be used with relatively high (lime/pozzolan mass ratio 1/2) ratios for the improvement of the mechanical properties of mortars if their pozzolanic activity is high. If the pozzolanic activity of the material is lower the upper limit of ratio that can be used to improve the mechanical properties of the mortar (Moropoulou 2005b).

Pozzolanic activity

One of the main considerations in selecting the pozzolanic material to be used in the preparation of mortars is the pozzolanic activity of the material in question. Several physicochemical characteristics such as the glassy compound content, the total and active silica content, the grain size distribution, specific surface area affect pozzolanic activity (Lea 1988). For artificial pozzolans parameters like clay quality, calcination temperature, the calcination process also influence the final activity (Sabir et al. 2001).

Although these properties are indicators of the pozzolanic activity, for the evaluation of the pozzolanic activity, the consumption of $Ca(OH)_2$ by the pozzolanic material taking place either in lime/pozzolan paste or in a solution of saturated $Ca(OH)_2$ is considered to be reliable method. When “lime/pozzolan paste” approach is used, known amount of $Ca(OH)_2$ is mixed with certain amount of pozzolanic material and water to form a paste. Then unreacted $Ca(OH)_2$ after a definite time is determined by an analytical method such as

TGA to assess the pozzolanicity of the material (Roszczynialski 2002, Moropoulou 2004). The extent of consumption of $Ca(OH)_2$ by the pozzolanic material can also be determined in a saturated solution of $Ca(OH)_2$. In that case, known amount of pozzolanic material is introduced in the solution, then after a definite amount of time, the unreacted $Ca(OH)_2$ is determined directly by a chemical method or by an indicator of the $Ca(OH)_2$ concentration like electrical conductivity (Luxan et al. 1989). In both methods the less amount of unreacted $Ca(OH)_2$, the more the pozzolanic activity. In cement research, the evaluation of pozzolanic activity is performed using an indirect method. The compressive strength of standard cement mortar samples is compared with mortars prepared by replacing certain percent of the cement by the pozzolanic material.

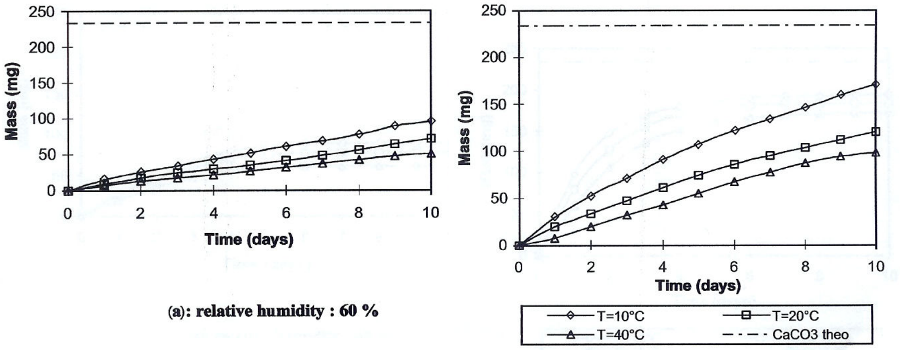
Metakaolin as a pozzolanic material

Thermal activation of many clay minerals at 600-900 °C leads to the breakdown or partial breakdown of crystal structure by dehydroxylation and forming of a highly reactive transition phase. Metakaolin ($Al_2O_3.2SiO_2$) is produced by the calcination of clay or lateritic soils rich in kaolinite (Pera et al. 1987). Reaction of metakaolin and $Ca(OH)_2$ in the presence of water forms a cementitious aluminium containing CSH gel, together with crystalline products, including calcium aluminate hydrates and alumino-silicate hydrates (C_2ASH_8, C_4AH_{13} and C_3AH_6). Metakaolin is known to have high pozzolanic activity. The activity of the produced metakaolin greatly depends on the kaolinite content of the clay. Clays rich in kaolinite have the best potential for activation to be used as a pozzolanic material (Chakchouk et al. 2006, Moroupoulou 2005b, Agarwal 2006). Calcining temperature of clays also affects the pozzolanic activity of the resulting product. The calcining temperature for activation of the kaolinite is usually in the range 600-800 ºC (Ambroise et al. 1986). Also calcination of kaolinite at temperatures below 700 ºC results in less reactive metakaolin with more residual kaolinite (Ambroise et al. 1986). Above 850 °C crystallization occurs and reactivity decreases.

1.2 Carbonation and pozzolanic reactions in lime mortars

1.2.1 Carbonation in lime mortars

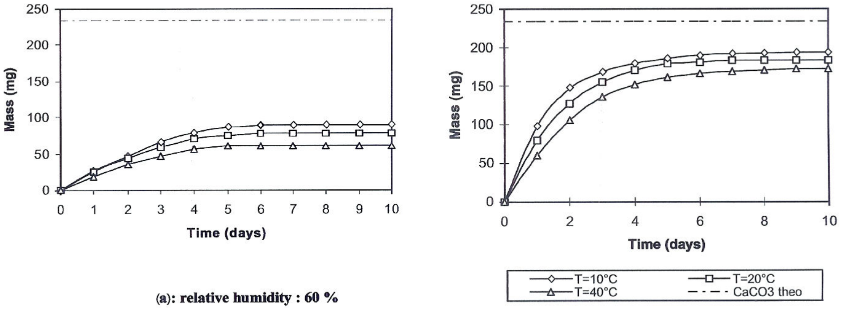
The reaction of carbonation can be explained by a two-stage reaction. First atmospheric CO_2 is dissolved in water forming H_2CO_3 and then H_2CO_3 reacts with the $Ca(OH)_2$ to form $CaCO_3$. (Van Balen, Van Gemert 1994). Since the reaction takes place in the solution, water must be present at all times. The rate of carbonation is directly related with the availability of the water inside the mortar system. Since for the reaction to proceed, CO_2 is essential, the availability of this reactant is also very important for carbonation. Thus to model the reaction kinetics of a mortar system, the carbonation process should be divided into two steps in which CO_2 diffusion takes place to the reaction site and a chemical reaction forming $CaCO_3$ crystals. Since the diffusion of CO_2 is 10000 times slower in water than in air, carbonation reaction is fully retarded when the material is saturated with water. In a mortar system the optimum water content for carbonation is the water content that corresponds to maximum adsorption on the surfaces of the pores before capillary condensation (Van Balen , Van Gemert 1994). The diffusivity of gaseous carbon dioxide in air depends on the openness of the porous structure and thus on the presence of water in the pores. Because of the fact that the diffusivity of CO_2 in air is much larger than in water it can be excluded as a transfer mechanism. The diffusion resistance will be related to the amount of water present in the mortar system and also to the speed of water production due to carbonation. But water production due to carbonation becomes crucial only when the reaction is accelerated at elevated CO_2 concentrations. The heat evolved during the carbonation reaction on the other hand is enough to evaporate the water content and leading to the premature set of mortar without complete carbonation if the available water content is limited (Morehead 1986). So relative humidity also has an effect on the rate of carbonation in mortars because of its relation with the water content of the mortar system. As the relative humidity increases the rate of water loss inside the mortar will be retarded so carbonation will continue.



(a): relative humidity : 60 %

(b): relative humidity : 100 %

Figure. 1.1 Effect of relative humidity on carbonation of $Ca(OH)_2$ in dry powder form. Y axis shows the weight increase of 661 mg dry Ca(OH)2 due to carbonation through ten days (Dheilly et al. 2002).



(a): relative humidity : 60 %

(b): relative humidity : 100 %

Figure 1.2 Weight increase of dry powder $Ca(OH)_2$ through ten days in a CO_2 rich atmosphere (Dheilly et al. 2002).

The rate and the range of carbonation are also influenced by the thickness of the mortar which is directly related with CO_2 transfer pathway. As the reaction proceeds, formed calcium carbonate makes the mortar less permeable to carbon dioxide leading to a decrease in the rate of carbonation.

Temperature is also another important factor for the carbonation reaction. The solubility of the carbondioxide decrease with increasing temperature, on the other hand, rate of chemical reactions increase with increasing temperature. The optimum temperature for the carbonation reaction is found to be 20 by Grandet 1975. In a recent study by Dheilly et al. in 2002, carbonation of dry powdered $Ca(OH)_2$ observed to be better at 10 °C compared with carbonation at 20 °C and 40°C (Fig 1.1-1.2).

1.2.2 Pozzolanic reactions

When lime and pozzolan mixtures are mixed with water first the solution reaches a high pH value by the dissolution $Ca(OH)_2$ as Ca^{2+} and $(OH)^-$, silicate or alumino-silicate network formers also dissolve into solution. Depolymerised monosilicates and aluminate species enter the solution as $[SiO(OH)_3]$ and $Al[OH]^-$ in that high pH solution. When Ca^{2+} ions come into contact with those species, CSH and CAH (C_4AH_{13}) are formed (Shi, Day 2000, Da Silva, Glasser 1993).

Dissolved monosilicate species diffuse much more quickly than alimunate species and higher concentration of Ca^+ is needed for the formation of calcium aluminate hydrates (CAH) than for calcium silicate hydrates (CSH). Hydrated calcium aluminates precipitate away from the pozzolanic particles and hydrated calcium silicates precipitate around the pozzolan particles. Shi and Day used some chemical activators Na_2SO_4 and $CaCl_2$ (4% solution) for the activation of pozzolanic reactions in lime pozzolan mixtures casted in cylindrical moulds (diameter 25 mm x 50mm) and investigated the reaction products by XRD and SEM analyses (Shi and Day 2000). By the addition of those activators, they observed a change in the formation of CSH and CAH proportions evaluated by XRD analyses. The results showed that when CAH formation was high, lime pozzolan pastes showed a higher strength than control samples and that fact could be explained by the mentioned fact that CAH precipitates away from the pozzolan particles so pozzolans were free to be in contact with the basic solution of $Ca(OH)_2$, thus the pozzolan continues to dissolve into the solution resulting the formation of new CAHs. That in fact led to increase in the solid volume of the system much more than the situation where the pozzolanic reaction product is CSH. By the continual increase in the solid volume, the structure becomes densified causing an increase in the strength values of the pastes. On the contrary, the production of the CSH takes place around the pozzolan particles, and as the reaction proceeds, availability of the pozzolanic material decreases. Although Shi and Day used activators to alter the course of pozzolanic reactions, their study showed how different reaction products from pozzolanic reactions change the final properties of lime pozzolan systems. But it must be also considered that in lime and pozzolan mixtures the formed CAH and CASHs were thought to be metastable phases that are formed in the early stages of curing which then convert to hydrogarnet after long periods of time (Da Silva, Glasser 1993).

1.3 Aim of the study

The main purpose of this study is to develop an understanding on the physical and mechanical properties of mortar mixtures prepared with several pozzolanic materials to prepare compatible and durable mortars for the repair of historic masonry. Investigation of some historic masonry mortars that have proved their compatibility and durability in time, are of special importance to gain information, such as their technological properties, performance and raw material characteristics, to be used as a guide for the preparation of the pozzolanic lime mortars for utilization in repair works. With the help of the information gathered by the examination of historic masonry mortars and literature about lime mortars, several mortar designs with various pozzolanic materials were tested and their characteristics were studied. The purpose of this study is not to develop a particular type of repair mortar for a specific case, but rather to understand how different pozzolanic materials affect the final characteristics of the lime mortars. By means of studying the changes in the physical and physicomechanical properties of mortars by the use of several pozzolanic additives, knowledge about how to prepare repair mortars with varying characteristics were tried to be widened. The information is thought to be also useful for the design of mortars that can be used for the purpose of historic stone repairs such as sticking scales, filling the gaps of deteriorated stones e.g. limestones, marbles, sandstones, etc.

CHAPTER 2

EXPERIMENTAL METHODS

The main purpose of this study was to investigate the effects of pozzolanic materials on the characteristics of lime mortars such as their microstructural, physical and physicomechanical properties. That information would be useful for the design of compatible and durable mortars for the repair of historic masonry. Also by utilizing that information, pozzolanic lime mortars for the repair of stones in historic structures, i.e. limestone, sandstone, marble, can be designed.

In the scope of the study, some historic masonry mortars were investigated. Limestone masonry mortars from a historic castle in the proximity of Nemrut Dağ Monument were selected, since these mortars have proved their functionality and durability in time and therefore would be a source of information to be used as a starting point for the preparation of repair mortars. Thus, mortars from limestone rubble masonry of Kahta Castle in the close vicinity of Nemrut Dağ Monument were analyzed.

Lime mortar mixtures with different pozzolanic additives with varying ratios were prepared and analyzed.

The preparation and analyses of lime mortar mixtures with pozzolanic additives were planned and put in practice by the knowledge gained through the analyses of historic mortars and recent literature about lime mortars.

Investigation of the effect of the pozzolanic materials and compositions of raw materials was performed on mortar cubes prepared by using lime, different aggregates and several pozzolanic materials. Mortar mixtures were casted in 5 cm cubic moulds and kept in a chamber with a relative humidity of 90% for curing. Tests were performed after 28, 60, 90 and 120 days of curing time.

Basic physical properties of bulk density, effective porosity, water vapour permeability, water impermeability and water absorption by capillarity of mortars were investigated. The hydric dilatation behaviour of mortars prepared by using different pozzolans was also examined.

Physicomechanical properties of modulus of elasticity were determined by ultrasonic pulse velocity measurements and uniaxial compressive strength by point load tests.

Mineralogical and petrographical characteristics of historic mortars were examined to find out their compositional properties in terms of binder, aggregates and additives. For those purposes, thin sections of the mortars were analyzed by using optical microscopy, cross sections of the samples were examined by SEM-EDX and powdered mortar samples were analyzed by XRD.

The unreacted $Ca(OH)_2$ was determined to investigate the extend of $Ca(OH)_2$ consumption, carbonation and pozzolanic reactions for the prepared pozzolanic lime mortars. XRD analyses were performed for the determination of the reaction products of carbonation and pozzolanic reactions together with the unreacted $Ca(OH)_2$ prepared lime mortar mixtures. SEM-EDX analyses were used to observe the pozzolanic reaction and carbonation products in the prepared pozzolanic lime mortars.

2.1 Sampling and nomenclature of the Kahta Castle mortars

Large mortars bulks from around the limestone walls of Kahta Castle were taken as samples. The samples are denoted as KM (Kahta Mortars) and numbered from 1 to 4. These bulk mortars were cut into appropriate sizes for the tests to be conducted and designated with the same code as the bulk they were cut from.

2.2 Preparation of the repair mortar mixtures

Several sets of mortars were prepared to analyze the development of their physical, physicomechanical properties and microstructural characteristics. Nomenclature of the mortar mixtures were as follows.

The first two letters represented the type of mortar i.e. RM: repair mortar, first and second letter after the dash designated the pozzolanic material (N: none, M: metakaolin, F: fly ash, B: brick powder) and aggregate type (S: standard sand, C: Cendere river sand) respectively. The last letter denoted the lime:pozzolan:aggregate ratio (C: 1:0:2, X: 1:0.5:2, Y: 1:1:1, Z: 1:0.4:0.6).

For the repeatability of the repair mortar mixtures, materials used such as binder, aggregates and pozzolanic materials, their proportions, water content and flow rate of the mixtures were specified.

2.2.1 Materials used

For the preparation of repair lime mortar mixtures, following raw materials were used.

The binder: Chemical $Ca(OH)_2$ (Sigma-Aldrich) was used as the binder in all mortar mixtures.

Aggregate: Two types of aggregates were studied in mortar mixtures; river sand from Cendere River and standard sand (EN 196-1). The particle size distribution of Cendere river sand and standard sand is shown in Figure 2.1.

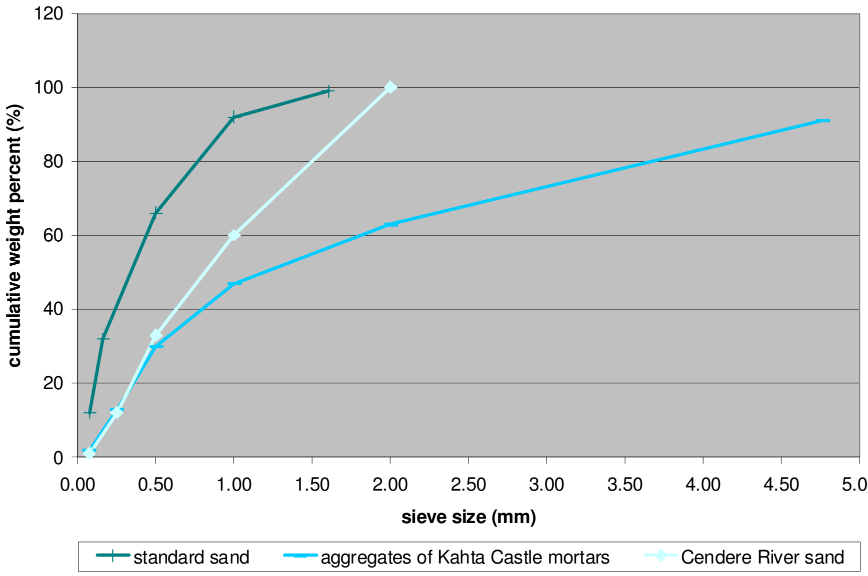


Figure 2.1 Particle size distribution of standard sand and Cendere River sand used in the preparation of repair mortar mixtures.

Standard sand used for the cement mortar strength tests was utilized in the preparation of pozzolanic lime mortars to eliminate the effect of aggregates to the final mortar characteristics. Cendere river sand with particle sizes up to 2 mm were used in the preparation of some of the repair mortars, considering the possible application of those mortars for filling the small sized cracks and gaps of limestone monuments of the Nemrut Dağ Monument.

Pozzolanic additives: Pozzolanicity of various materials obtained from different sources; fly ash, grounded bricks from Ördekli Hamam, Bursa, metakaolin, an artificial pozzolan prepared in the laboratory by burning kaolinite were used.

Fly ash used was from Tunçbilek Thermal Power Plant. It contains high amounts of reactive oxides classified as Class F fly ash (ASTM C618) with low CaO content. Brick powder was prepared by grinding bricks from a historic bath, Ördekli Hamam, Bursa.

Metakaolin was prepared in the laboratory by heating pure kaolinite (Sigma-Aldrich) at a degree of 700 ºC for 24 hours. The conversion of kaolinite into metakaolin by heating at 700 ºC was verified by comparing XRD traces of kaolinite and calcined kaolinite. In general kaolinite gives identification peaks at *d* values 7.15 Å (001) and 3.57 Å (002). When heating kaolinite at temperatures above 550 ºC, collapse of structure to an X-ray amorphous mineral takes places and metakaolin is produced. However a peak of kaolinite with weak intensity at about 1.49 Å can be observed (Carroll 1970).

$$\underset{\text{kaolinite}}{Al_2O_3.2SiO_2.2H_2O} \xrightarrow{700\ ^\circ\mathrm{C}} \underset{\text{metakaolin}}{Al_2O_3.2SiO_2} + H_2O$$

In this study the kaolinite used had definite characteristic peaks at 7.15, and 3.57 which disappeared after heating showing that it was converted to metakaolin. Those changes were followed in XRD traces shown in Fig 2.1.

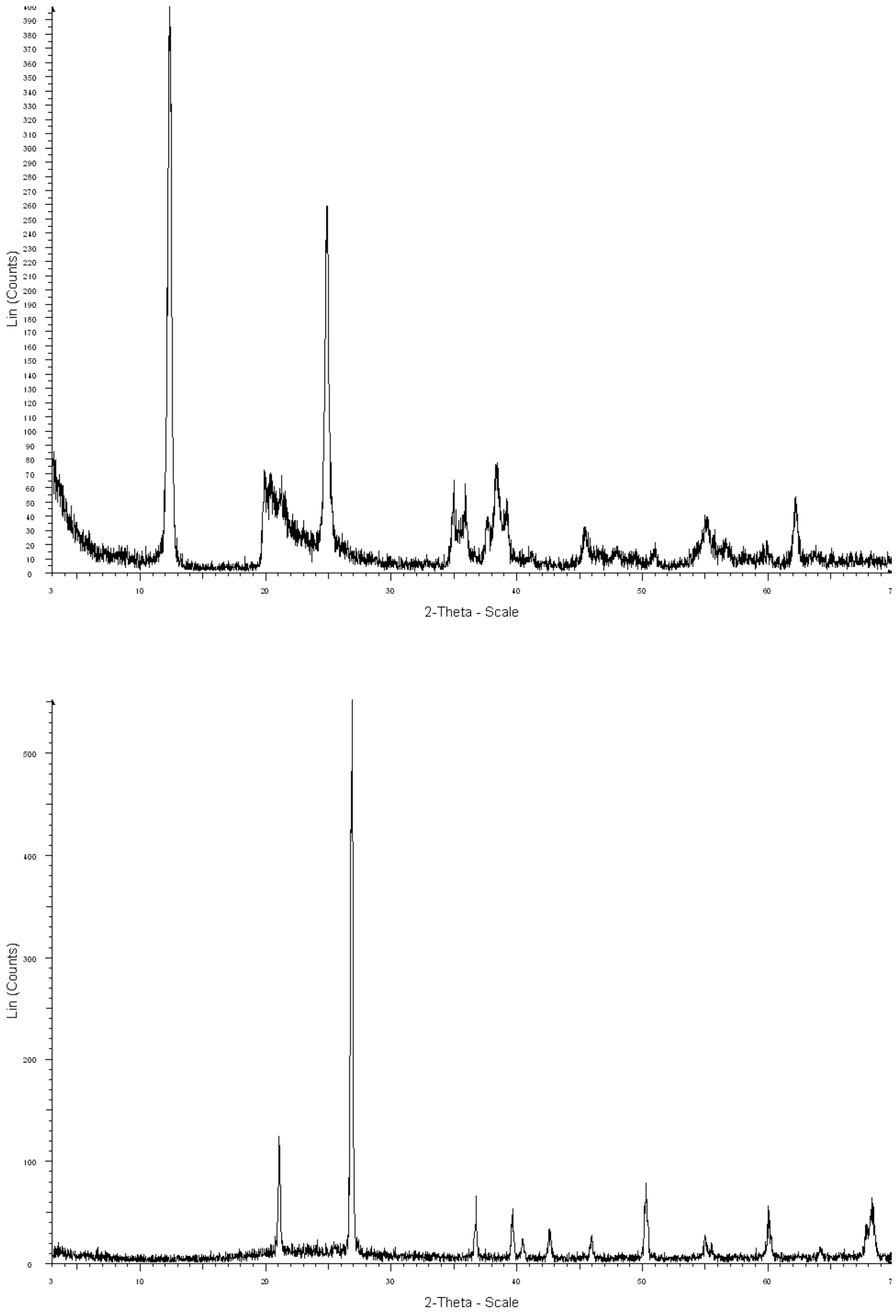


Figure 2.1 XRD trace of kaolinite (above;) and metakaolin (below)

Pozzolanic activity determination of the pozzolanic materials was described in section 2.6.3 of this chapter.

For the preparation of the lime putty, 1000 g of $Ca(OH)_2$ was mixed with 1000 ml of water. The mixture was kept in a closed container for three days to mature. Then, the prepared lime putty was mixed with aggregates and selected pozzolanic material. Additional water was added to the mixture in order to have a workable consistency. The prepared mixture was tested for consistency with the flow test (ASTM C1437-07). Adequate water was added to the mixtures to have a flow of 70% ±10. Then the mortar mixtures were casted in 5 cm cubic bakelite moulds. The mortar cubes were demoulded after two days. Different sets of lime mortars that were prepared with different pozzolanic materials and proportions were shown in (Table 2.1).

Table 2.1. Prepared pozzolanic lime mortars

Sample*	Curing times(days)	Number of cubes	Pozzolan used	Lime:pozzolan:aggregate	Aggregate	Flow %
RM-NS-C	28, 60, 90	24	no pozzolan	1:0:2	Standard sand	60
RM-MS-X	28, 60, 90	24	metakaolin	1:0.5:2	Standard sand	71
RM-FS-X	28, 60, 90	24	fly ash	1:0.5:2	Standard sand	68
RM-BS-X	28, 60, 90	24	brick powder	1:0.5:2	Standard sand	71
RM-MC-Y	60, 90, 120	12	metakaolin	1:1:1	Cendere river sand	74
RM- MC-Z	60, 90, 120	12	metakaolin	1:0.4:0.6	Cendere river sand	66

For the curing of the mortar mixtures a test chamber with a wooden frame and polyethylene covering was used. Mortar mixtures were kept in that chamber at a relative humidity of 85% ±5 by placing open water containers inside (Figure 2.2). The chamber was kept in the laboratory at a temperature of 20 ±2 °C.

Figure 2.2 Some of the prepared pozzolanic lime mortars and the chamber.

2.2.2 Flow rate determination of repair mortar mixtures

Flow rate of the prepared mortar mixtures were tested according to ASTM C1437-07 by using a flow table in order to obtain a consistent workability among the different sets of mortars. Tests were conducted by placing the mortar mixture in a conical brass meld on the flow table. The mould was then removed and the table was mechanically dropped through a height of ~1.25 cm, 25 times in 15 seconds. The initial and final diameters of mortar mixture were used to calculate flow. The "flow" of the mortar was reported as a percentage increase from the initial diameter. The flow, thus the consistencies of the prepared mortars was kept 70±5% by adding adequate amount of water. Flow rates of the repair mortars mixtures were shown in Table 2.1.

2.3 Determination of basic physical properties of mortars

Basic physical properties of historic mortars from Kahta Castle and repair mortars at different curing times were determined. The physical properties determined were bulk density, effective porosity, water vapour permeability, water impermeability, water absorption by capillarity, hydric dilatation. Repair mortars were also followed for their shrinkage behaviour during curing. The experimental procedures for the conducted tests were briefly described below.

2.3.1 Determination of bulk density and effective porosity

Historic mortar samples were oven dried at 60 °C and repair mortar cubes that were cured for different periods of time were oven dried at 105 °C for 24 hours to constant weight. Their dry weights were recorded (M_{dry}).

The samples were then saturated with ethyl alcohol in a vacuum chamber (Heraus vacuum chamber) since the $Ca(OH)_2$ was insoluble in ethyl alcohol. Then, ethyl alcohol saturated weight of samples were recorded as saturated weights (M_{sat}). Samples were then weighted in ethyl alcohol to obtain their Archimedes weight (M_{arch}). Those weights were then used in the calculation of bulk density and effective porosity of the samples (RILEM 1980; Teutonico 1986). The same procedure was used for historic mortars by using water.

Porosity (P) is the total volume of pores or empty spaces in the mass of a porous material. It is expressed as a percentage of volume by the following formula (RILEM, 1980).

$$P\ (\%) = [(M_{sat} - M_{dry})/(M_{sat} - M_{arch})] \times 100$$

where,

M_{sat} : saturated weight (g)
M_{dry} : dry weight (g)
M_{arch} : weight of sample in liquid (ethyl alcohol) (g)

Bulk density is the ratio of the mass to the apparent volume of the sample and is calculated by the following formula and expressed in g/cm^3 (RILEM, 1980).

$$D\ (g/cm^3) = M_{dry} / [(M_{sat} - M_{arch}) / d_{ethyl\ alcohol}]$$

where,

$d_{ethyl\ alcohol} = 0.790\ g/cm^3$

2.3.2 Determination of shrinkage during setting

The volume change of mortars were determined by taking three dimensional measurements after initial casting, 90 days of curing time in order to evaluate the shrinkage in volume of mortar cubes during setting as percent volume. The results are presented as final volume / initial volume x 100.

2.3.3 Determination of water vapour permeability

Determination of water vapour permeability was performed by the wet-cup method (RILEM). For this test, a cylindrical container sample was used for each sample. The thickness of the sample was measured from four different points and average value was calculated as thickness (S_0). Container was filled with water leaving 2 cm air space above water surface. Then the top of the container was covered with the sample and edges were sealed with melted paraffin. The sample was weighted and initial weight was recorded. Relative humidity, atmospheric pressure of the laboratory were measured and recorded. The test sample was weighed periodically until the weight change per unit time due to evaporation of water became constant.

Following equation was used for the calculation of water vapour permeability.

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

where,

SD : equivalent air thickness of 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

2.3.4 Determination of water impermeability

Determination of water vapour impermeability of mortar samples was adopted from TS EN 539-1. For the test, the samples were cut to a thickness of 2.5 cm. Open ended graduated cylinders were sealed on the surfaces of the samples to be tested. Mortars were then saturated with water for 24 hours before testing. Then the cylinders were filled with water. The volume of water that has passed through the mortar in 24 hours was recorded. The water evaporated from the cylindrical graduated cylinders was also recorded by observing a reference cylinder filled with water. Impermeability factor was calculated by the following equation (TS EN 539-1 modified) as $cm^3/(cm^2 d)$.

$$IF = (V1 - V2) / A$$

where,

V1 : volume of water passed through the sample
V2 : volume of water evaporated from the reference cylinder
A : water-sample contact area

2.3.5 Determination of hydric dilatation

Hydric dilatation test were conducted by performing hydric expansion coefficient measurements. For the measurements a system having a dilatometric displacement sensor LVDT (linear variable differential transformer) were used. Samples to be tested were cut into rectangular prisms with the dimension of 1.0 x 1.0 x 5.0 cm. Samples were oven dried at a temperature of 105 ºC for 24 hours, then cooled to ambient temperature (20 ºC ±1) and partly immersed in water to measure the hydric dilatation. The measurements were carried out until no dilatation was observed. The results were expressed in mm/m.

2.4 Determination of physicomechanical properties of historic mortars and repair lime mortars

Physicomechanical properties of both historic mortar samples and repair mortars were expressed as modulus of elasticity and point load strength calculations as described below. The effects of the different pozzolanic materials and curing time on the physicomechanical properties of the repair mortars were then evaluated.

2.4.1 Determination of modulus of elasticity

The modulus of elasticity of the samples was calculated by using their direct ultrasonic velocity and bulk density in a proper equation. Ultrasonic velocity of the mortar cubes were measured by using a ultrasonic velocity measurement device (PUNDIT Plus) with 220 KHz probes. The ultrasonic velocity was calculated by using the formula,

$V = l/t$

where,

V : velocity (m/s)
l : distance traversed by the wave (m)
t : time (s)

Modulus of elasticity values were then calculated by using ultrasonic velocity values and bulk density of the mortar cubes with the equation:

$$E_{mod} = D.V^2.(1 + V_{dyn})(1 - 2V_{dyn}) / (1 - V_{dyn})$$

where,
E_{mod} : modulus of elasticity (MPa)
D : bulk density of specimen (kg/m^3)
V : wave velocity (m/s)
V_{dyn} : Poisson's ratio

Poisson's ratio varies from 0.1 to 0.5. In this study, it was taken as 0.18 as a value used for historic mortars (Timenshenko 1970, Topal 1995, Tuncoku 2001)

2.4.2 Determination of the uniaxial compressive strength by point load measurements

Point load tests were performed on historic mortar samples and prepared repair mortar cubes for the estimation of their uniaxial compressive strength by using an ELE-point load test apparatus. Following procedure was used in the calculation of uniaxial compressive strength. First uncorrected point load strength index (Is) for mortar were calculated by using the formula,

$Is = P/De^2$

where,

P : applied force (kN)
De : equivalent core diameter (mm)

Equivalent core diameter (De) is calculated by the formula,

$De = (4A/\Pi)^{1/2}$

where A is the minimum cross sectional area of the test specimen.

Size-corrected point load strength , $Is_{(50)}$ is calculated by using uncorrected point load strength index, Is, using equivalent core diameter method with the following equation (Brook 1985),

$Is_{(50)} = F \times Is$

Where F, the size correction factor calculated from equivalent core diameter, De, by the equation,

$F = (De/50)^{0.45}$

For the calculation of uniaxial compressive strength from the Is_{50}, following equation is used based on a study on weak tuffs (Topal 1999, 2000).

$$UCS = 10.6471 \times Is_{50} + 2.4736$$

The uniaxial compressive strength results were expressed in MPa.

2.5 Determination of the free $Ca(OH)_2$ content in the mortars

For the determination of the free $Ca(OH)_2$ content in the repair mortar cubes, complex forming titrations with standard EDTA solutions prepared from disodium ethylene diamine tetra acetate was used as an analytical technique. After the predetermined curing times, cubes were oven-dried at a temperature of 105 °C for 24 hours to constant weight. Then the cubes were cut in half. The outer and the inner part of the cubes were scratched and the powder obtained was used for the determination of the free $Ca(OH)_2$ content in the outer and inner parts of the cube. Powder samples of 0.2 grams were weighted accurately and put into a 100 ml volumetric flask and mixed with distilled water for the free $Ca(OH)_2$ to dissolve into solution. The solutions were then used for the analyses of free $Ca(OH)_2$ content by volumetric titration with EDTA. The pH of the solution was adjusted to 12-13 by using 10% NaOH solution and calcon indicator was used for the titrations (Black 1965).

2.6 Determination of raw material characteristics of historic mortars

Raw material characteristics such as the nature of binder, aggregates and pozzolanic materials of historic mortars were investigated by the determination of acid soluble/insoluble parts, particle size distribution of aggregates, pozzolanic activity tests, thin section analyses by optical microscopy, SEM analyses coupled with EDX and XRD analyses. The pozzolanic activity tests, thin section analyses by optical microscopy, SEM analyses coupled with EDX and XRD analyses explained in this section were also performed for the analyses of repair mortars to follow carbonation and pozzolanic reactions during the course of curing.

2.6.1 Determination of acid soluble and insoluble parts of historic mortars

Acid insoluble parts represent the aggregates that were insoluble in acid. However some aggregates that may be present in the mortars might be acid soluble. Combined interpretation of thin section and SEM-EDX analyses should be used to better evaluate binder/aggregate ratio and particle size distribution of mortars.

Determination of the acid soluble/insoluble parts of historic mortars was performed by treating an oven dried sample with 5% HCl acid to dissolve the binder. The acid insoluble part were then filtered and washed until free from chloride ions and dried in an oven at about 40 °C until constant weight. The difference in the initial weight and acid insoluble weight were then used to calculate the acid soluble and insoluble parts as a weight percent.

2.6.2 Determination of particle size distribution of acid insoluble parts of historic mortars

The acid insoluble parts of mortar samples were sieved through a series of sieves with mesh sizes of 1000 µm, 500 µm, 250 µm, 125 µm (DIN-4188). Then mass of particles retained on each sieve were recorded and cumulative percentages were graphically represented. In case there were some acid soluble aggregates in the mortar, particle size distribution of the mortar should better be estimated by investigating the acid soluble aggregates in terms of their sizes and approximate amounts through the analyses of thin sections.

2.7 Determination of pozzolanic activity

Pozzolanic activity tests were performed on the pozzolans used for the preparation of the pozzolanic lime mortars and on the acid insoluble parts of historic mortars having particle sizes below 125 µm. For the pozzolanic activity test 0.02 gram of sample were put in a container having 30 ml saturated solution of calcium hydroxide. The container is then closed and left in laboratory conditions for 8 days. The solution is then titrated with a 0.01 M EDTA (ethylene diamine tetra acetic acid) solution. The solution pH is kept at 12-13 during the titrations by using a solution of NaOH (10%). Calcon indicator was used for the titration. Because pozzolanic materials react with and consume Ca^{2+} ions, the difference between the Ca^{2+} ion concentration of the saturated solution of $Ca(OH)_2$ and the concentration after the 8 day period gives information about the reactivity of the pozzolan. The activity is expressed as the mg $Ca(OH)_2$ consumption of 1 gram of test sample.

2.8 Mineralogical and petrographical properties of mortars

Mineralogical properties of both historic mortars and repair mortars were examined by thin section analysis with optical microscopy, SEM-EDX and XRD analyses of samples.

2.8.1 Thin section analysis

For thin section preparation, samples were cut into adequate sizes and epoxy resin was impregnated into the samples to fill the pores and mechanically support the specimen. Then hardened epoxy impregnated samples were cut into slices and glued on glass slides and grinded until a thickness of 30 µm was achieved. Thin section analyses were performed with a Leica 4500 research microscope. Mineralogical and petrographical properties of binder and aggregates were examined.

2.8.2 Scanning electron microscopy (SEM) coupled with energy dispersive X-ray detector (EDX)

SEM analysis aimed to provide complementary information about morphology and microstructure of binder and aggregate parts and possible reaction products formed by carbonation and pozzolanic reactions. Mortar samples of about 3 cm with a flat surface was prepared and coated with carbon before the SEM-EDX analyses. The instrument used was a Tescan Vega II XMU with large chamber coupled with an OXFORD INCA energy dispersive X-ray analysis (EDX) system by which elemental analysis can be done. SEM images were taken and elemental analyses were carried out and evaluated together with the images.

2.8.3 X-Ray diffraction analyses

X-Ray diffraction analyses were used to determine the mineralogical phases and the binder in historic lime mortars and to observe the formation of $Ca(CO)_3$, pozzolanic reaction products and unreacted $Ca(OH)_2$ by using the instrument Bruker D8 Advance Diffractometer with Sol-X detector. Analyses were done using CuKα radiation, adjusted to 40 kV and 40 mA. The XRD traces were recorded in the 3° - 70° 2θ range. Samples scratched from the outer and the inner surfaces of the mortar cubes were also used for the XRD analyses to see the extend of carbonation and pozzolanic reactions in the outer and inner surfaces of the mortar cubes.

CHAPTER 3

EXPERIMENTAL RESULTS

Results of analyses performed on historic mortars and prepared repair mortars described in the experimental methods were presented in this chapter. The results of basic physical properties; bulk density and effective porosity, water vapour permeability, water impermeability, hydric dilatation behaviour and physicomechanical properties of modulus of elasticity, uniaxial compressive strength tests of historic mortars and repair mortars were given.

Results of analyses on the raw material characteristics of historic mortars such as acid soluble/insoluble contents, nature of binder and aggregates, pozzolanicity of the fine aggregates as well as the results of pozzolanic activity tests of the pozzolans used in the preparation of repair mortars, microstructural examinations, mineralogical and petrographical analyses, SEM-EDX and XRD analyses of both historic mortars and repair mortars were presented.

3.1 Basic physical properties of historic mortars and repair mortars

3.1.1 Bulk density and effective porosity

Bulk density and effective porosity of the pozzolanic lime mortars prepared with metakaolin, fly ash and brick powder through 28 to 90 days are shown in Figure 3.1.

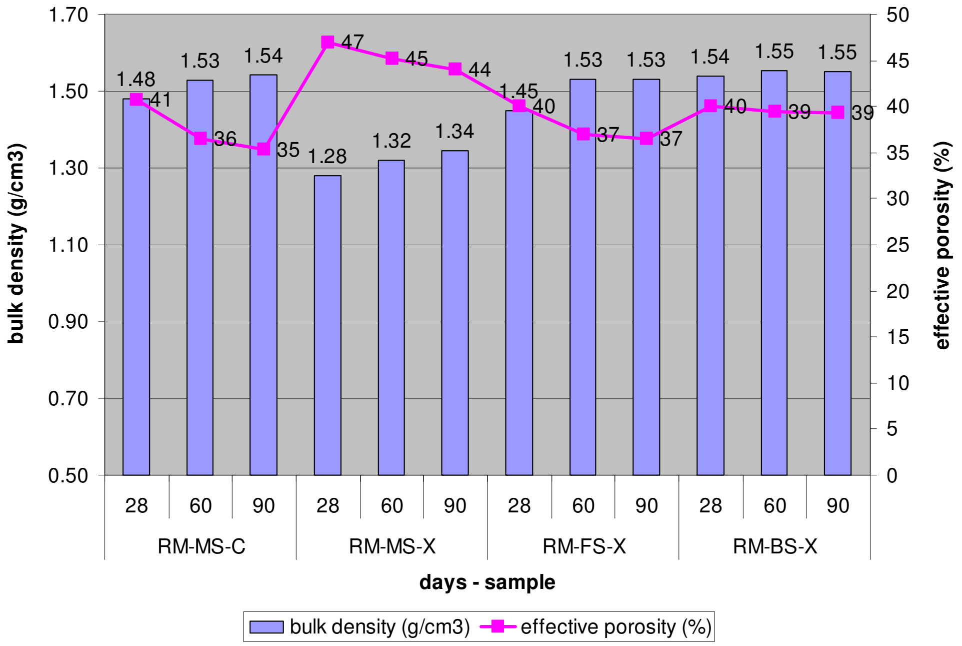


Figure 3.1 Bulk density and porosity of the repair mortars, RM-MS-X, RM-FS-X, RM-BS-X and control, RM-NS-C.

Bulk densities of the prepared pozzolanic lime mortars varied between 1.34-1.55 g/cm^3 and porosities between 37-44% at the end of 90 days of curing period. Mortars prepared with added metakaolin showed the lowest bulk density and highest porosity 1.34 g/cm^3 and 44% percent respectively. Mortars prepared with fly ash and brick powder showed similar bulk density values in the range of 1.53-1.55 g/cm^3 with a porosity range of 37-39%. The density of the control group was 1.54 g/cm^3 and the porosity was 35%. Bulk density values of all mortars were observed to have a slight increase between 28 and 60 days and porosity values had a slight decrease in the same period. The increase in bulk density was less pronounced between 60 and 90 days. Porosity values of all mortars were decreased as the curing time increased.

RM-MC-Y pozzolanic lime mortars which were prepared with a 1:1:1, lime:metakaolin:aggregate ratio were observed for their bulk density and effective porosity change in time (Fig 3.2). A set of those mortar cubes were left on site at Nemrut Dağ Monument for a period of 120 days for comparison with the mortars that were cured in the relative humidity chamber in the laboratory. The average bulk density of the mortar cubes that were kept in the laboratory were 1.09 g/cm^3 and the average porosity were 42% at the end of 120 days. The mortar cubes that were left on site for 120 days had a bulk density of 1.03 and porosity of 53%.

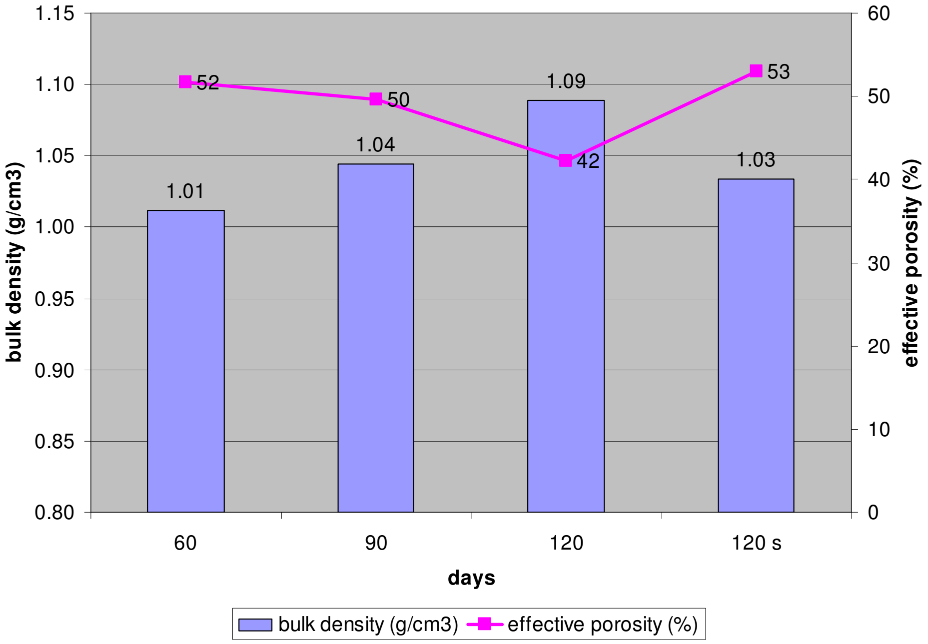


Figure 3.2 Bulk density and porosity change in repair mortars, RM-MC-Y at 60th, 90th and 120th days in the laboratory. (120 s: denotes the mortars left on site at Nemrut Dağ Monument for 120 days.)

The bulk density and porosity change of RM-MC-Z mortars which had a lime:metakaolin:aggregate ratio of 1:0.4:0.6 is shown in figure 3.3 from day 28 to day 90. the bulk density of the mortars at the end of 90 days were 1.1 g/cm^3 and the porosity were 54%.

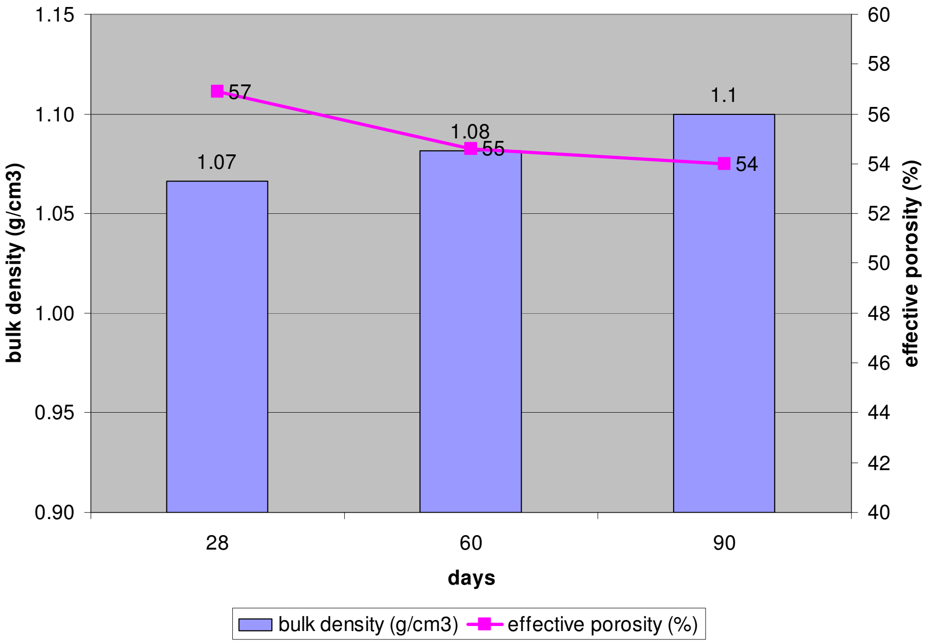


Figure 3.3 Bulk density and porosity change in repair mortars, RM-MC-Z at 28, 60 and 90 days in the laboratory.

Bulk density and porosity of Kahta Castle mortars

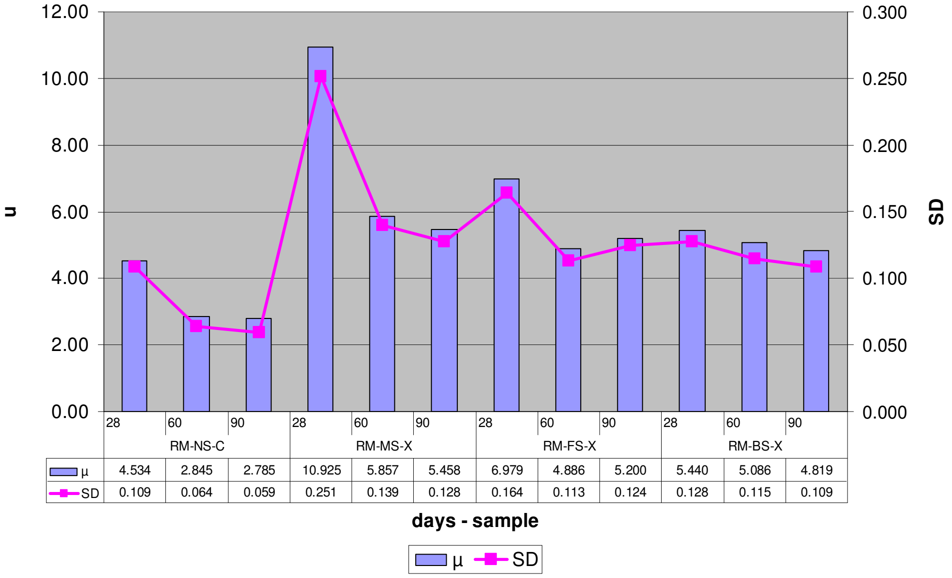
Kahta Castle mortars had an average bulk density of 1.69 g/cm^3 and an average porosity of 35.3%.

Table 3.1 Bulk density and effective porosity of Kahta Castle mortars.

Sample	Bulk density (g/cm3)	Effective porosity (%)
MK1	1,71	35
MK2	1,72	34
MK3	1,68	36
MK4	1,65	36
MK avg	1,69±0.3	35±1

3.1.2 Water vapour permeability

Water vapour permeability of the prepared lime mortars is shown in figure 3.4. SD values of the pozzolanic lime mortars were in the range of 0.109-0.128 compared with SD value of 0.059 of control samples when the thickness of the mortars were about 2.5 cm. μ values varied between 4.819-5.458. Mortars prepared with metakaolin were observed to have the highest SD and μ at the end of 90 days. Control sample without any pozzolanic additive had the lowest SD and μ values. All pozzolanic lime mortars had high water vapour permeability at the end of 90 days according to the classification denoted in the standard TS EN 1062, 7783 (Table 3.2).



	28	60	90	28	60	90	28	60	90	28	60	90
	RM-NS-C			RM-MS-X			RM-FS-X			RM-BS-X		
μ	4.534	2.845	2.785	10.925	5.857	5.458	6.979	4.886	5.200	5.440	5.086	4.819
SD	0.109	0.064	0.059	0.251	0.139	0.128	0.164	0.113	0.124	0.128	0.115	0.109

Figure 3.4 SD and μ values of prepared repair mortars, RM-MS-X, RM-FS-X, RM-BS-X and control, RM-NS-C.

Average SD value for Kahta Castle mortars was 0.111 and μ value was 5.343 which were in the high water vapour permeability class according to TS EN 1062, 7783.

Table 3.2 Classification of water vapour permeability according to TS EN 1062, 7783

Classification	SD (m)
1. High	<0.14
2. Medium	0.14-1.4
3. Low	>1.4

3.1.3 Water impermeability

Results of water impermeability tests conducted according to the standard TS EN 539-1 are shown in Figure 3.5. According to the standard TS EN 1304, a first class water impermeable layer should have an impermeability coefficient less than 0.6 cm^3/cm^2d. A second class water impermeable layer should have an impermeability coefficient less than 0.9 cm^3/cm^2d.

Mortars prepared with fly ash showed the lowest impermeability coefficient 0.02 cm^3/cm^2d whereas control samples without any pozzolanic additive showed highest impermeability coefficient when they are tested approximately with a thickness of 2.5 cm at the end of 90 days curing time. The IF factor of mortars with metakaolin and mortars with brick powder are 2.88 and 0.30 cm^3/cm^2d respectively. A slight decrease in water impermeability factor between 28 and 60 days were observed on pozzolanic lime mortars. No significant change in water impermeability factor is seen between day 60 to day 90 on mortars. The average IF value of Kahta Castle mortars were 6.7 cm^3/cm^2d.

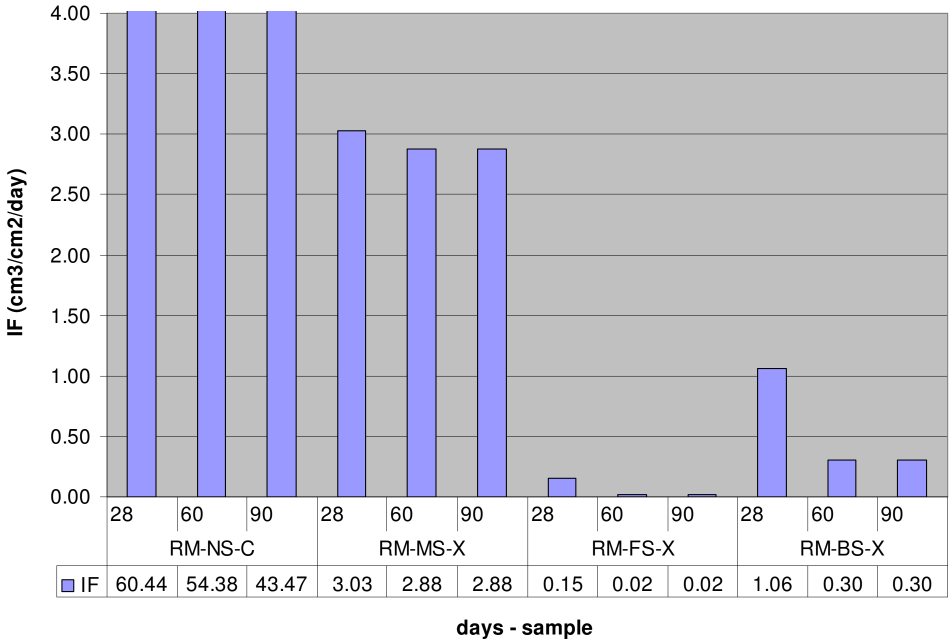


Figure 3.5 Impermeability coefficient of repair mortars, RM-MS-X, RM-FS-X, RM-BS-X and control, RM-NS-C.

3.1.4 Hydric dilatation

The results of hydric dilatation tests are shown in Figure 3.6. The hydric dilatation was observed higher on mortars prepared with metakaolin with a value of 0.689 mm/m. The least dilatation in pozzolanic lime mortars were detected on mortars with added brick powder, with 0.041 mm/m. Hydric dilatation of fly ash added mortars were 0.223 mm/m. For the control samples, when the sample tested were in contact with water, disintegration of the samples was observed so the recorded dilatation values were negative. The wet compressive strength tests for the control could not be performed because of the same reason.

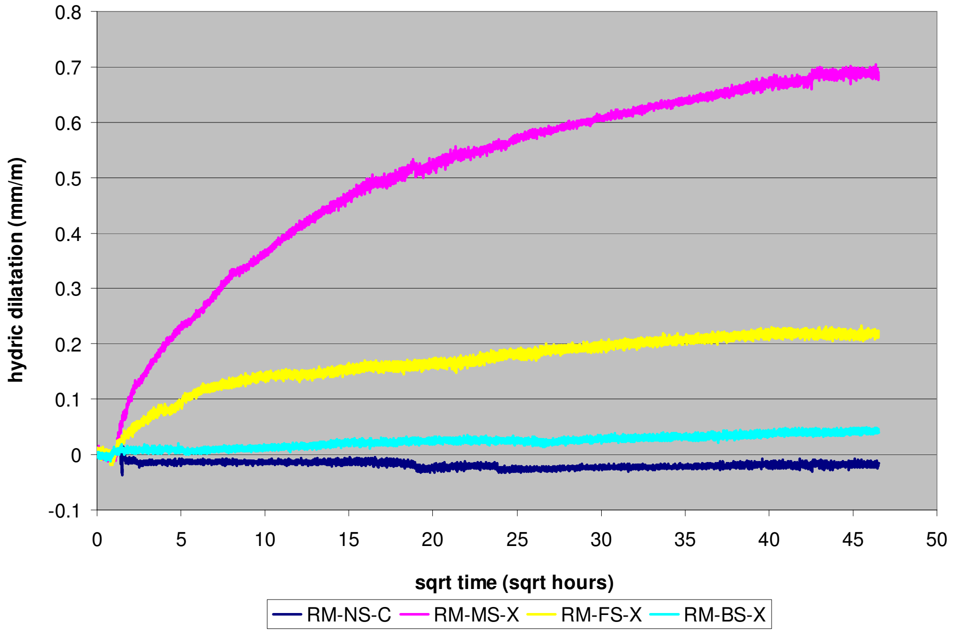


Figure 3.6 Hydric dilatation of repair mortars (RM-MS-X, RM-FS-X, RM-BS-X and control (RM-NS-C).

3.1.5 Shrinkage of repair mortars during setting

The shrinkage percentages of repair mortars at the end of 90 days of curing time is shown in Table 3.3.

Table 3.3 Shrinkage percentages of repair mortars at the end of 90 days

Sample	Shrinkage (%)
RM-NS-C	8.3
RM-MS-X	4.5
RM-FS-X	6.4
RM-BS-X	4.5

3.2 Physicomechanical properties of mortars

3.2.1 Modulus of elasticity (E_{mod})

Ultrasonic velocity values of prepared pozzolanic mortars were between 1273-1838 m/s. Modulus of elasticity (E_{mod}) varied between 1999-4759 MPa at the end of 90 days. Highest values for both ultrasonic velocity and modulus of elasticity were observed in the mortars prepared with fly ash. Control sample showed the lowest values (Figure 3.7) with a ultrasonic velocity value of 946 m/s and modulus of elasticity of 1270 MPa.

Ultrasonic velocity values of RM-MC-Y mortars were 1505 m/s and modulus of elasticity were 2270 MPa at the end of 120 days. RM-MC-Y mortars which were kept at the site had an average ultrasonic velocity of 1173 and modulus of elasticity of 1310 MPa (Fig 3.8).

RM-MC-Z mortars were observed to have an ultrasonic velocity of 1001 m/s and modulus of elasticity of 1016 MPa at the end of 90 days of curing time (Fig 3.9).

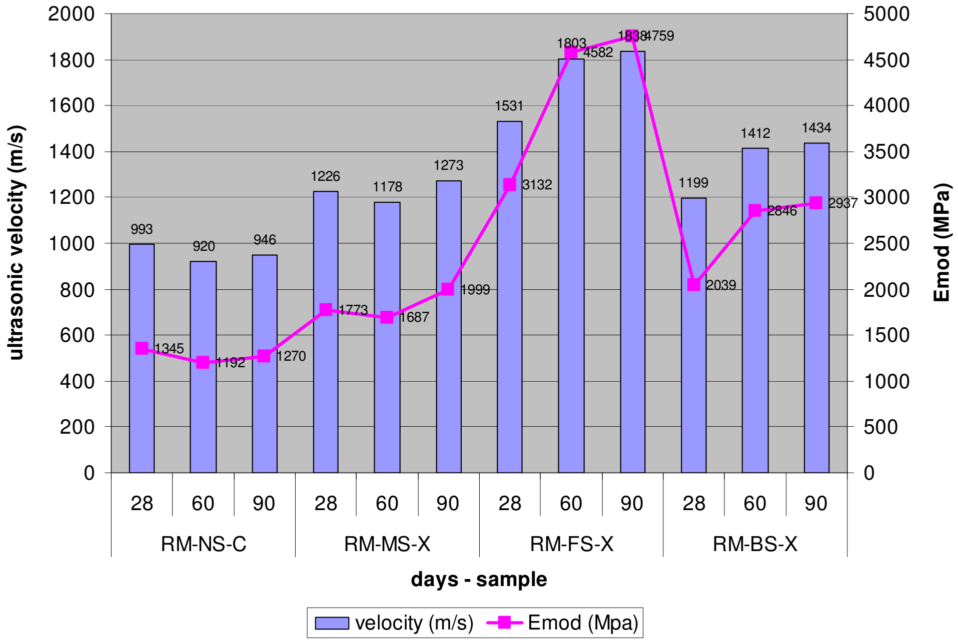


Figure 3.7 Ultrasonic velocity and modulus of elasticity values of repair mortars (RM-MS-X, RM-FS-X, RM-BS-X and control (RM-NS-C).

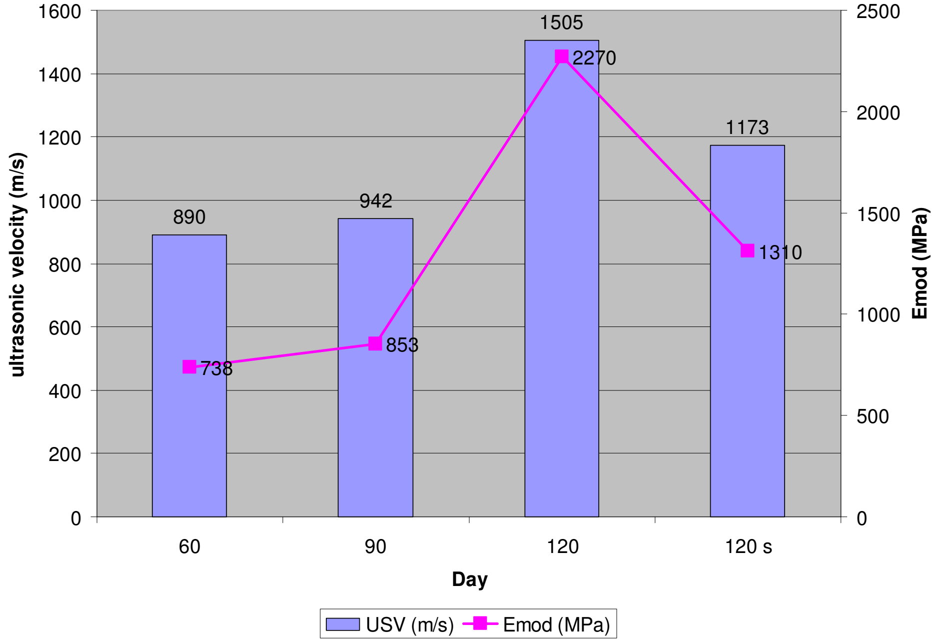


Figure 3.8 Ultrasonic velocity and modulus of elasticity values of prepared pozzolanic lime mortars RM-MC-Y from day 60 to day 120. 120 s denotes to mortars left outdoors on site.

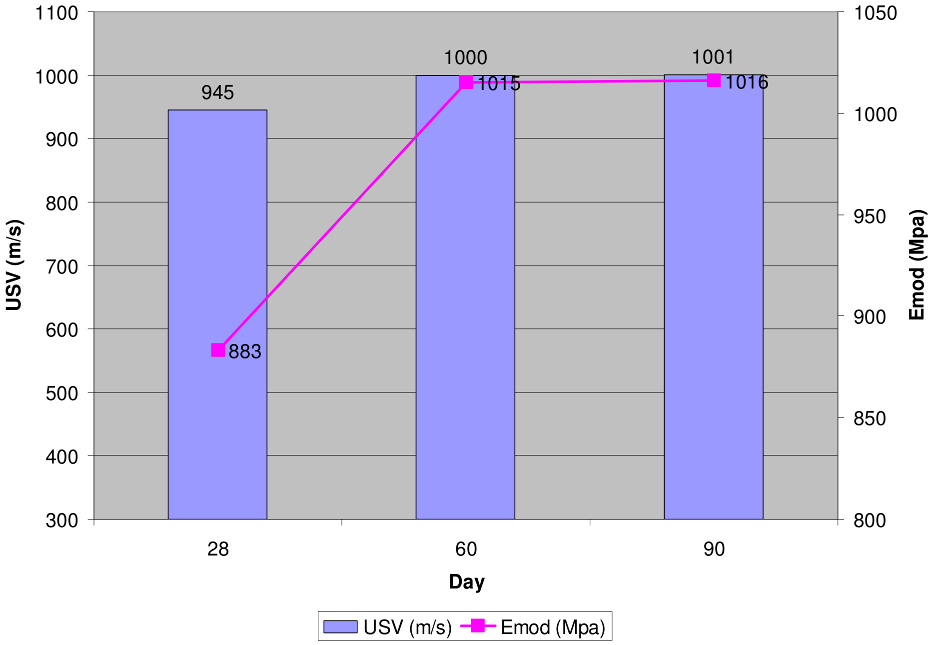


Figure 3.9 Ultrasonic velocity and modulus of elasticity values of prepared pozzolanic lime mortars, RM-MC-Z from day 28 to day 90.

Modulus of elasticity of Kahta Castle mortars

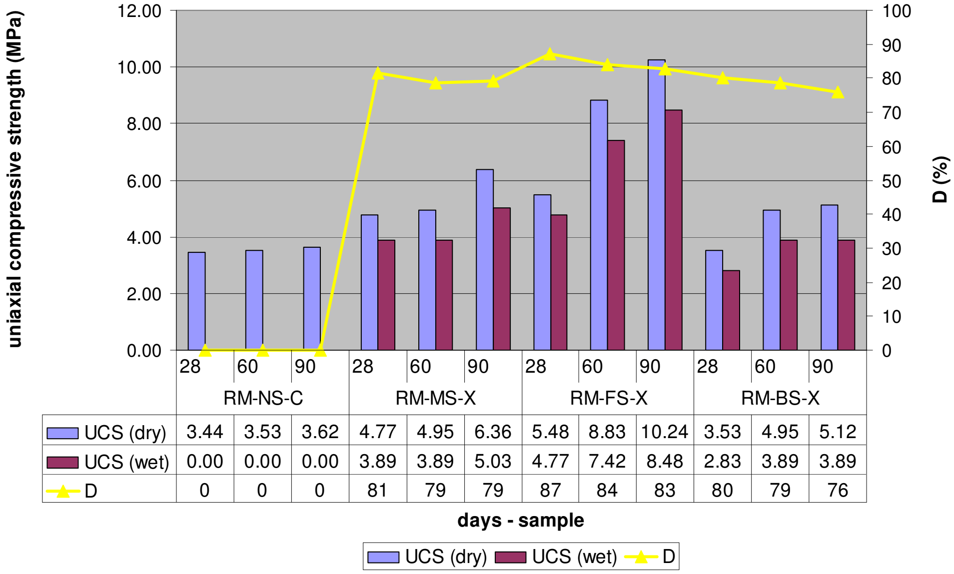
Kahta Castle mortars had an average ultrasonic velocity of 1851 m/s. Their average modulus of elasticity was 5423 MPa.

Table 3.3 Ultrasonic velocity and modulus of elasticity values of Kahta Castle mortars

Sample	USV (m/s)	Emod (MPa)
MK1	1928	5872
MK2	1854	5434
MK3	1781	5010
MK4	1844	5376

3.2.2 Uniaxial compressive strengths of mortars by point load measurements

Uniaxial compressive tests were conducted on dry and water saturated mortar cubes. Durability character of mortar samples were evaluated by using the dry and water saturated compressive strength values. The strength values of dry samples were in the range of 5.12-10.24 MPa at the end of 90 days. Water saturated strength values of mortars were between 3.89-8.48 MPa (Fig 3.10). The average dry compressive strength value of control samples were 3.62 MPa at the end of 90 days.



	RM-NS-C			RM-MS-X			RM-FS-X			RM-BS-X		
	28	60	90	28	60	90	28	60	90	28	60	90
UCS (dry)	3.44	3.53	3.62	4.77	4.95	6.36	5.48	8.83	10.24	3.53	4.95	5.12
UCS (wet)	0.00	0.00	0.00	3.89	3.89	5.03	4.77	7.42	8.48	2.83	3.89	3.89
D	0	0	0	81	79	79	87	84	83	80	79	76

Figure 3.10 Uniaxial compressive strength of repair mortars (dry and water saturated), D: UCS_{wet}/UCS_{dry} ratio.

Durability of the mortars was evaluated by calculating the durability factor, D (Winkler 1986) by the following equation.

$D = (UCS_{sat} / UCS_{dry}).100$

where,

UCS_{sat} : Uniaxial compressive strength (water saturated)
UCS_{dry} : Uniaxial compressive strength (dry)

As proposed by Winkler, the durability of rocks was evaluated in the following ranges according to their D values.

100-80 : excellent durability
80-70 : very good to good durability
70-60 : fair durability
60-50 : poor durability

According to this classification durability parameter of the lime mortars prepared with fly ash had excellent durability whereas mortars prepared with added metakaolin and brick powder were in the very good to good durability. Durability factor D could not be calculated for control samples for which water saturated compressive strength values could not be measured by using point load apparatus because of their disintegration in their wet state.

The uniaxial compressive strength tests of RM-MC-Y and RM-MC-Z mortars were conducted dry. RM-MC-Y mortars cured at the laboratory showed a compressive strength of 3.4 MPa at the end of 120 days while the ones left on site had a compressive strength of 5.1 MPa (Fig 3.11). RM-MC-Z mortars had a compressive strength of 4.1 MPa at the end of 90 days (Fig 3.12).

Uniaxial compressive strength of Kahta Castle mortars

Average uniaxial compressive strength of Kahta Castle mortars was 7.4 MPa.

Table 3.4 Uniaxial compressive strength of Kahta Castle mortars

Sample	Uniaxial comp. strength (MPa)
MK1	8,4
MK2	7,8
MK3	6,3
MK4	7,2

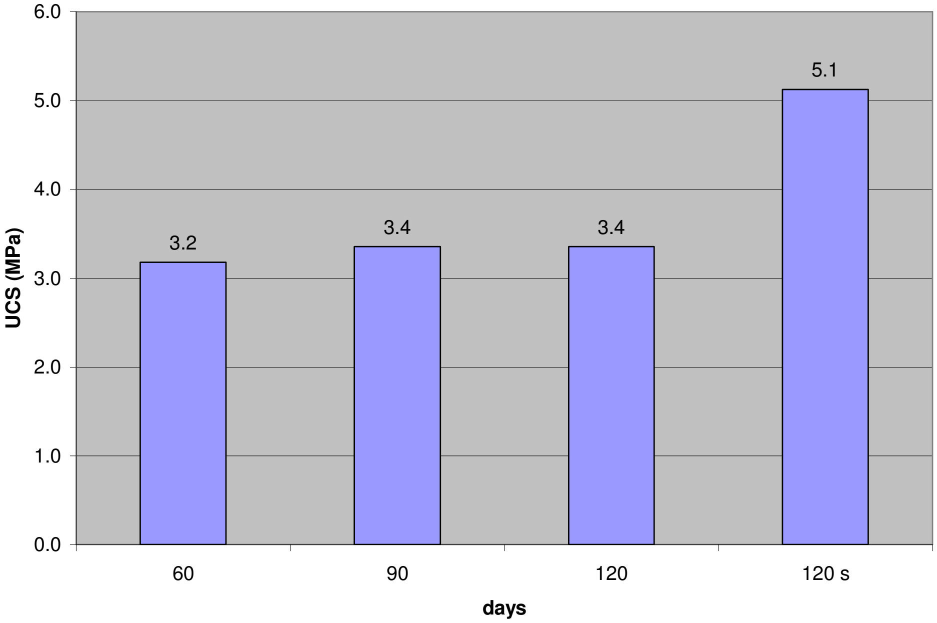


Figure 3.11 Uniaxial compressive strength of prepared pozzolanic lime mortars, RM-MC-Y from day 60 to day 120. 120 s denotes to mortars left outdoors on site.

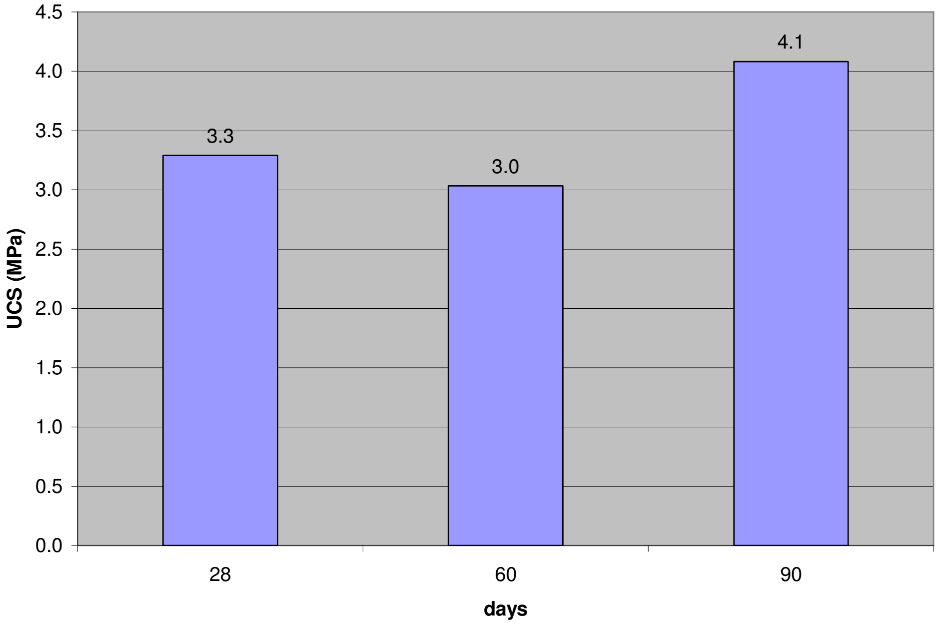


Figure 3.12 Uniaxial compressive strength of prepared pozzolanic lime mortars, RM-MC-Z from day 28 to day 90.

3.2.3 Free $Ca(OH)_2$ content in the prepared pozzolanic lime mortar cubes

Free calcium hydroxide content as weight percentage of the sample was calculated for both the outer surfaces (ext) and the inner core (in) of prepared lime mortars after 14, 28, 60 and 90 days of curing time. Figure 3.13 shows the results for all mortar sets.

In all mortar cubes, outer surface showed lower percentage of free calcium hydroxide content than the interiors. Lime mortar prepared with added metakaolin were observed to have the lowest free calcium hydroxide content in both outer and inner parts of the cubes at the end of 90 days. The free calcium hydroxide percent considerably decreased for the control and repair mortars with added brick powder from day 14 to day 28. For prepared lime mortars with added fly ash and metakaolin percentage of free calcium hydroxide did not show significant decrease between day 14 and day 28. The free $Ca(OH)_2$ percent decreased for all mortar set between day 28 to days 90 (Fig 3.13).

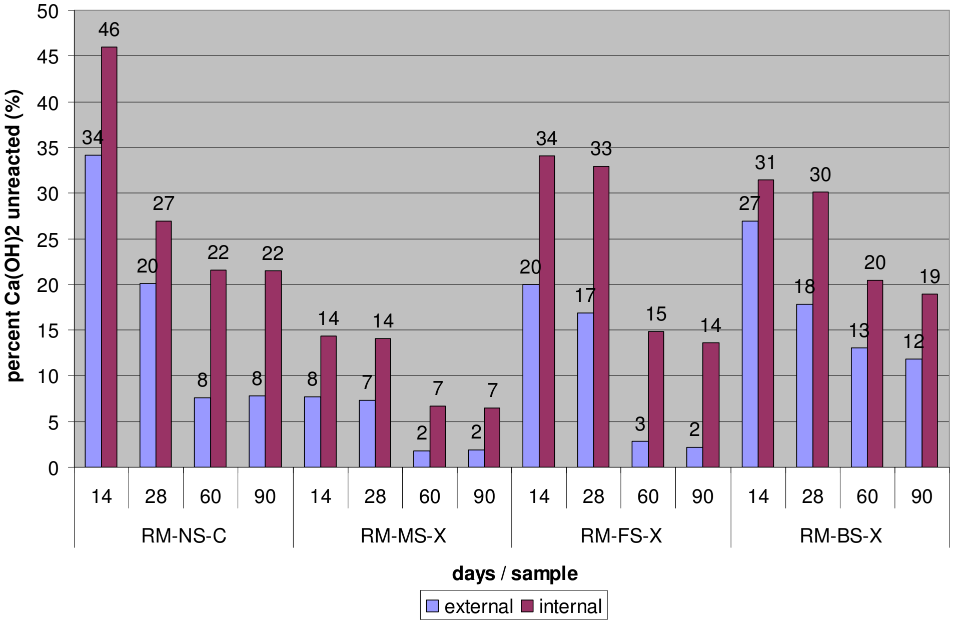


Figure 3.13 Free $Ca(OH)_2$ content in the repair mortars after 14, 28, 60 and 90 days.

3.3 Raw material characteristics of historic mortars

3.3.1 Acid soluble/insoluble parts and particle size distribution

Analyses of acid soluble/insoluble part of mortar samples from Kahta Castle showed that 37% of the mortar was acid insoluble. The results showed that the amount of binder could be at most 63%. Particle size distribution of acid insoluble part of the mortars was shown in Figure 3.14.

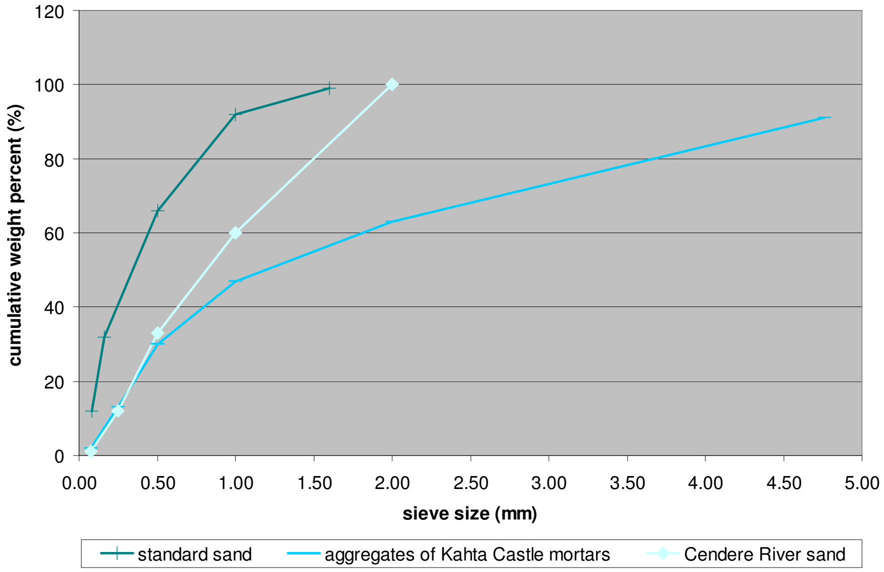


Figure 3.14 Particle size distributions of the acid insoluble parts of Kahta Castle mortars, standard sand and Cendere River sand used in the preparation of repair mortars

Particle size distribution of standard sand and Cendere River sand used as aggregates in the repair mortars were consisted largely of finer sized aggregates up to 2 mm.

The result of particle size distribution analyses showed that in Kahta Castle mortars more than 50% of the acid insoluble part consisted of aggregates with particle sizes greater than 1000 μ. Approximately 35% of the acid insoluble aggregates were in the range of 250-1000 microns and 15% was smaller than 250 micron. The aggregates of the latter were the ones that could react with lime to an extent that affect the final properties of the mortar because of their high surface area. To determine the pozzolanicity of the aggregates smaller than 125 microns, pozzolanic activity test was conducted.

3.3.2 Pozzolanic activity

Pozzolanic activity test were performed on both the pozzolans used for the preparation of the pozzolanic lime mortars and also for the acid insoluble aggregates of Kahta Castle mortars with particle sizes smaller than 125 µ. Results of analyses are shown in table 3.5.

Table 3.5 Pozzolanic activities of pozzolanic materials and aggregates (<125 µ) of Kahta Castle mortars.

Sample	ΔEC	mg $Ca(OH)_2$/g pozzolan
brick powder	2.1	30.7
fly ash	0.3	4.3
metakaolin	21.6	319.4
Kahta Castle mortar aggregates*	3.1	88.2

* aggregates <125 µ

The pozzolanic activity was expressed as mg calcium hydroxide consumption of 1 gram of pozzolanic material in 8 days. The decrease in the concentration of Ca^{2+} was also expressed in decrease in electrical conductivity to compare the results with the classification of Luxan et al. (Luxan 1989). Results showed that pozzolanic activity of metakaolin was the highest and fly ash is the lowest of the tested materials. The finer aggregates of the Kahta Castle mortars showed relatively high pozzolanicity.

3.4 Microstructural properties of mortars

3.4.1 Thin section analysis

Petrographical analyses of thin sections of mortar samples from Kahta Castle showed that radiolarite and various types of schist (muscovite-quartz, biotit-quartz) and serpentinite particles were in abundance. Quartzite, limestone and dolomitic limestone were also observed (Fig 3.15). Analyses of the thin sections also revealed the existence of the white lumps. The occurrence of white lumps was most probably due to insufficient mixing of slaked lime with aggregates. They were identified as micritic calcite crystals which did not mix with the binder matrix.

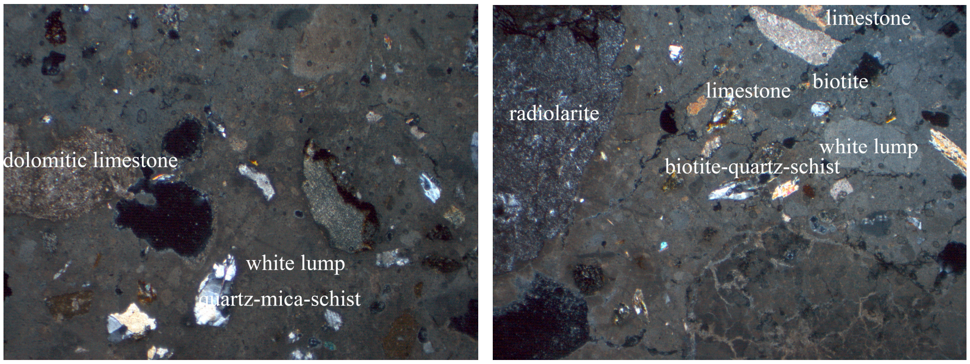


Figure 3.15 Thin section images of mortars from Kahta Castle (cross nicols 2.5x).

Thin sections of lime mortars prepared with using sand from Cendere river were also analyzed to compare the mineralogical and petrographical properties of the aggregates from Cendere river and those that were found in the historical mortars from Kahta Castle which was in the vicinity of Cendere River.

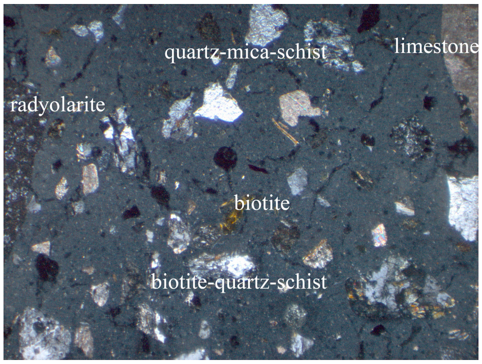


Figure 3.16 Thin section view showing the aggregates used for the preparation of pozzolanic mortars (cross nicols 2.5x).

Analyses of thin sections of mortars prepared with aggregates from Cendere River showed that radiolarite, serpentinite and schist were the common aggregates similar to the mortar samples from Kahta Castle. Limestone and quartzite were also observed both in historic and prepared mortars with Cendere River sand (Fig 3.16).

3.4.2 Scanning electron microscopy (SEM) coupled with energy dispersive X-Ray analyzer (EDX)

To determine the nature of binder SEM-EDX analyses were performed. SEM analyses of the binder matrix revealed the fact that average particle sizes of white lumps that were encountered during thin section analyses of the historic lime mortars were smaller than the particle size of the crystals in the binder matrix (Fig 3.17). Those fine aggregates of the micritic calcite crystals in the white lumps indicating the use of fat lime in historic mortars could also be considered as the evidence of the fine sized and thus plastic nature of the lime used in the historic mortars. SEM-EDX analyses revealed the presence of calcium and relatively small amount of magnesium confirmed the composition of the slaked lime used in the historical mortars as being fat lime (Fig 3.18).

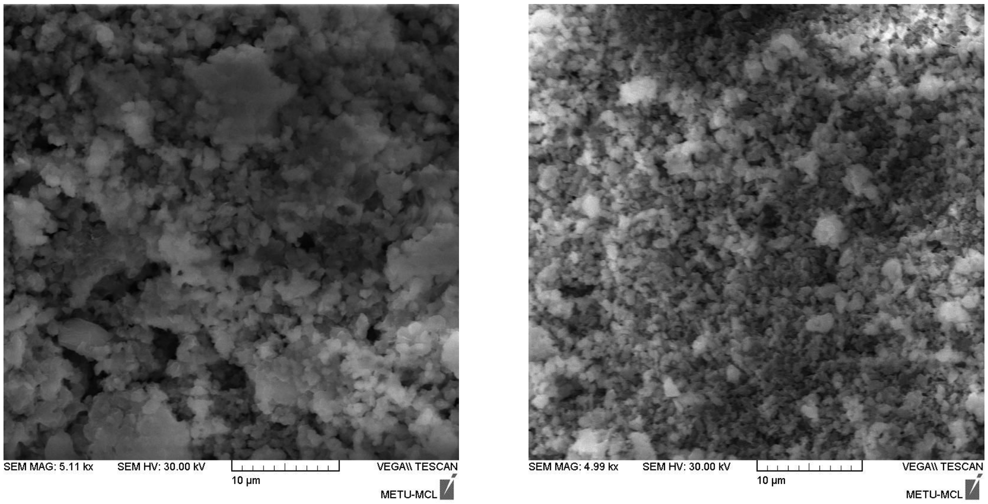


Figure 3.17 SEM image of binder matrix of mortar sample from Kahta Castle (left). White lump in the mortar matrix (right) showing the distinction between the particle sizes of the crystal aggregates in the binder matrix and the white lump.

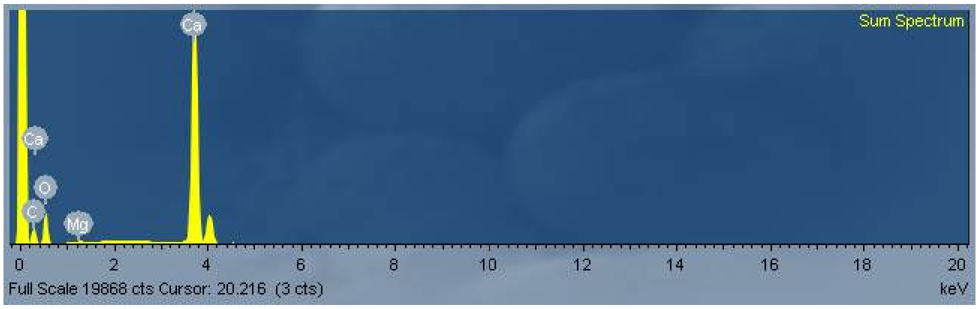


Figure 3.18 EDX analyses of the white lump in Kahta Castle mortars.

In the SEM analyses of the mortars with added metakaolin, needle like structures, possibly crystal phases from pozzolanic reactions, calcium aluminium silicate hydrate, CASH were detected (Fig 3.19). Result of spot EDX analyses of the needle like structure was shown in Figure 3.20. The EDX analyses confirmed that the structure was CASH.

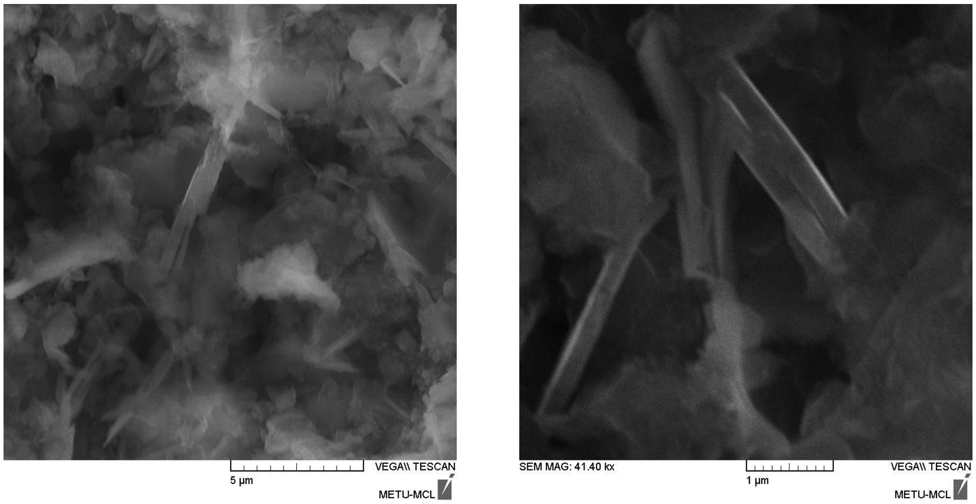


Fig 3.19 SEM image of needle like CASH formation from mortar prepared with added metakaolin (left).

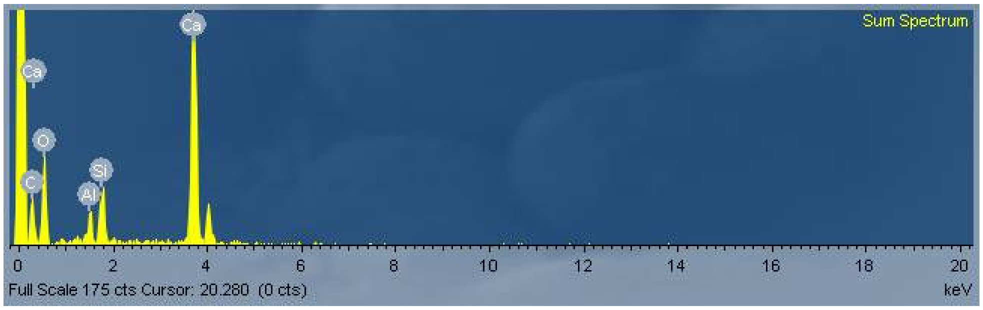


Figure 3.20 EDX analyses of needle like CASH structure.

3.4.3 XRD analyses

XRD analyses were performed on historic mortars for the determination of the mineralogical phases and on repair mortars to examine the changes in their mineralogical composition in time due to carbonation and pozzolanic reactions. Powdered mortar samples from Kahta Castle clearly showed the presence of calcite which confirmed that lime was used as the binder. Also quartz was observed as the main constituent of the aggregates in historic mortars(Fig 3.21).

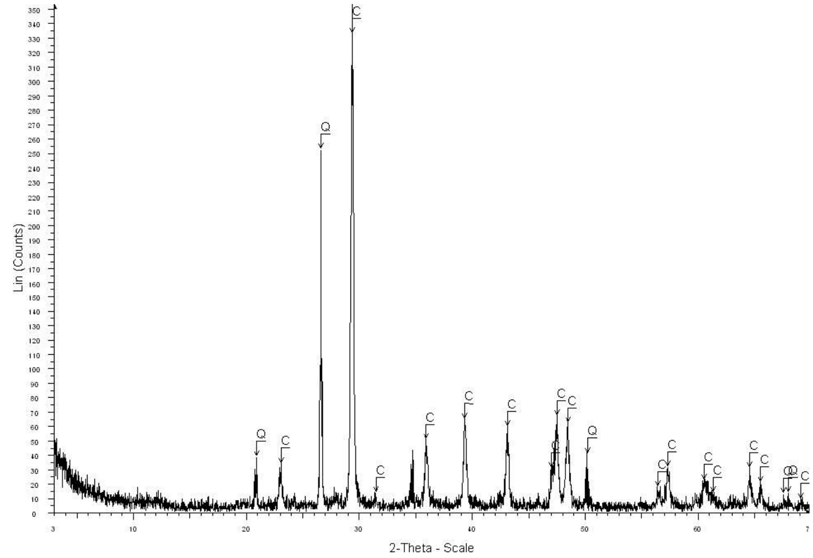


Figure 3.21 XRD traces of a mortar sample from Kahta Castle. C: Calcite, Q: Quartz

XRD analyses were conducted on the prepared pozzolanic lime mortars for the determination of carbonation and pozzolanic reaction products and the unreacted $Ca(OH)_2$. Powdered samples from both exterior surfaces and the inner cores of the mortar cubes were analyzed with XRD.

XRD traces of the internal and external surfaces of the prepared lime mortars from 28 to 90 days of curing time are shown in Figures 3.22-3.25.

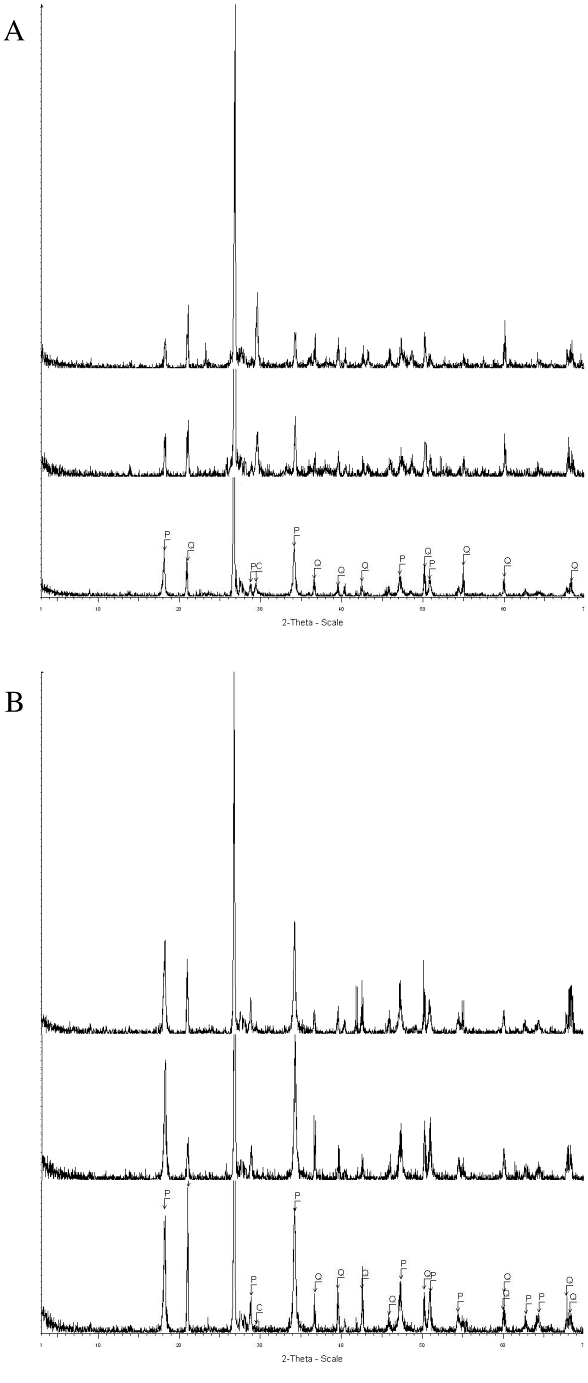


Figure 3.22 XRD traces of the mortar set, RM-NS-C after 28, 30 and 90 days (from bottom to top) of curing time (A external surface, B internal surface). C: Calcite, Q: Quartz, P: Portlandite

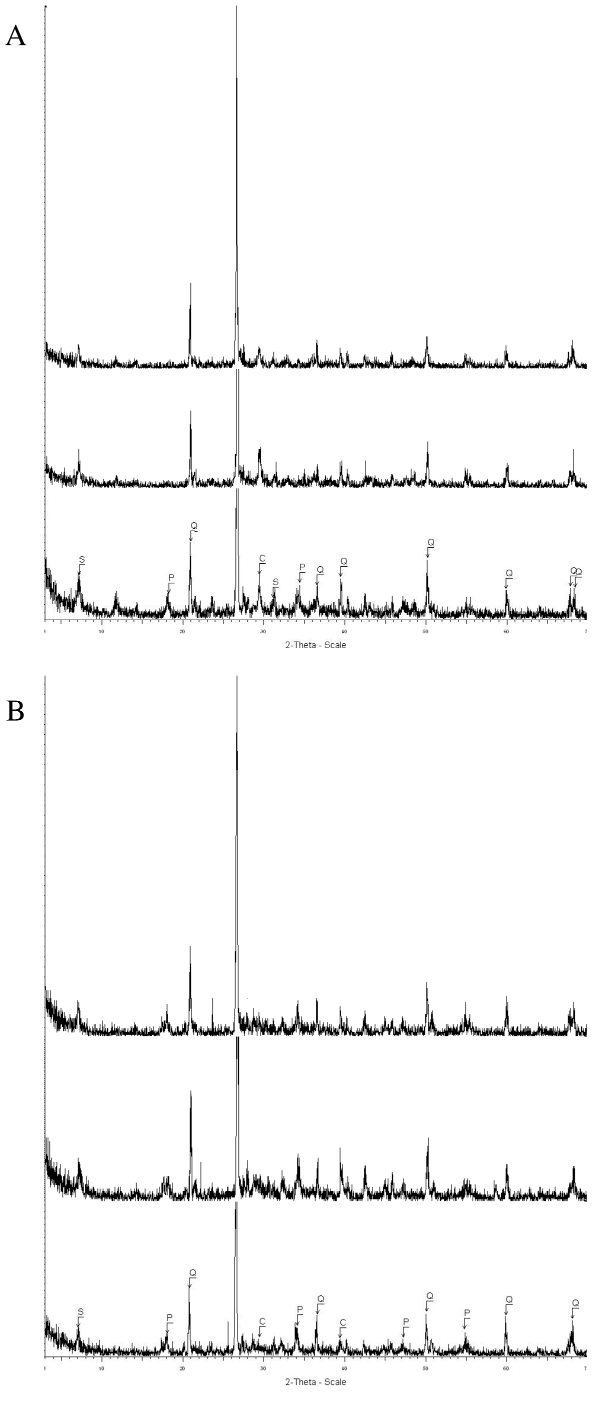


Figure 3.23 XRD traces of the mortar set RM-MS-X after 28, 30 and 90 days (from bottom to top) of curing time (A external surface, B internal surface below). C: Calcite, Q: Quartz, P: Portlandite

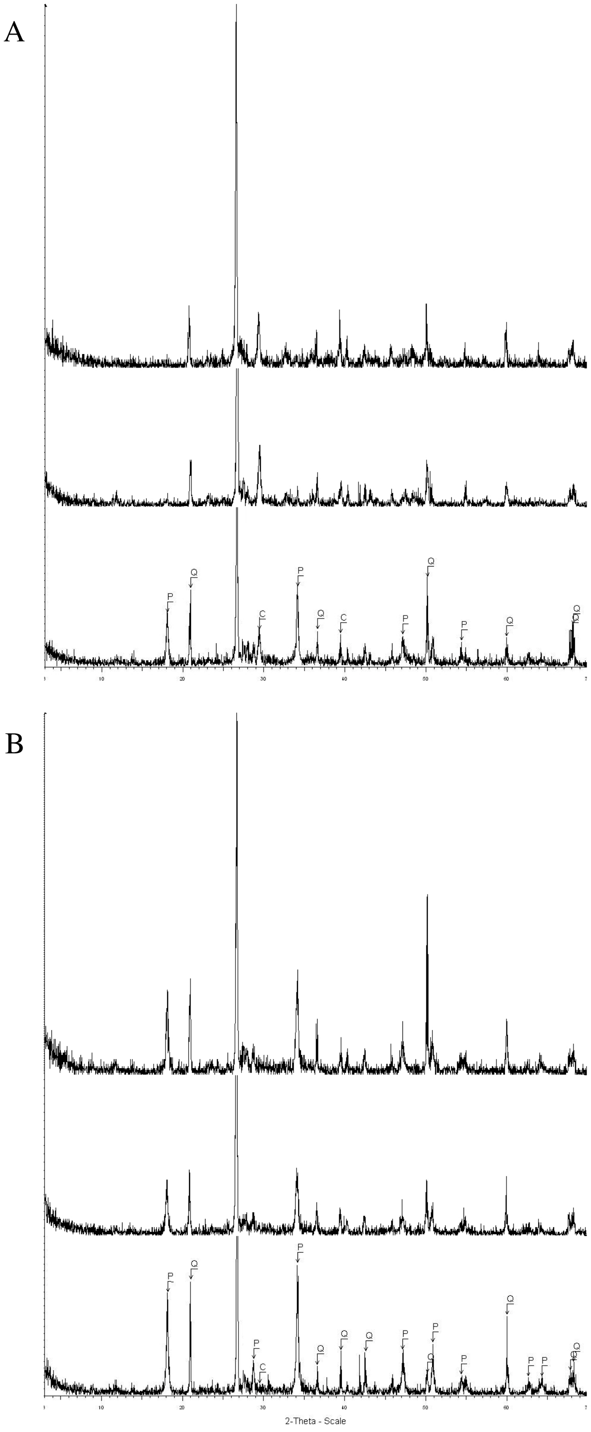


Figure 3.24 XRD traces of the mortar set RM-FS-X after 28, 30 and 90 days (from bottom to top) of curing time (A external surface, B internal surface). C: Calcite, Q: Quartz, P: Portlandite

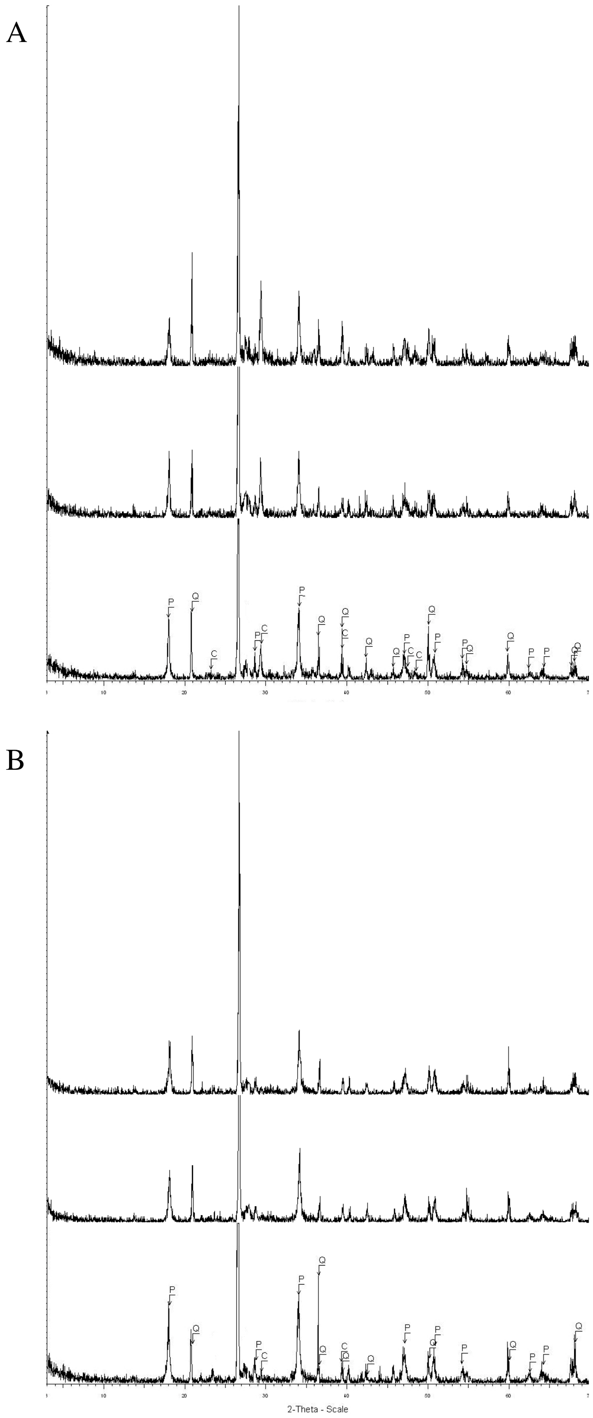


Figure 3.25 XRD traces of the mortar set RM-BS-X after 28, 30 and 90 days (from bottom to top) of curing time (A external surface, B internal surface). C: Calcite, Q: Quartz, P: Portlandite

Figure 3.26 shows the XRD traces of external surfaces of the RM-MC-Y mortar cubes. Stratlingite, the pozzolanic reaction product of metakaolin and lime can be clearly identified in the mortar cubes cured at the laboratory. Calcite peak as a result of carbonation were also identified. Almost all $Ca(OH)_2$ observed to be used by carbonation and pozzolanic reactions confirmed by the lack of portlandite peaks. Although stratlingite peak had high intensity in the XRD traces of mortar cubes cured at the laboratory, calcite was dominant in the mortar cubes left on site. Increase in the intensity of the calcite peak in time showed that development of calcite steadily continued and became significant at the end of 120 days.

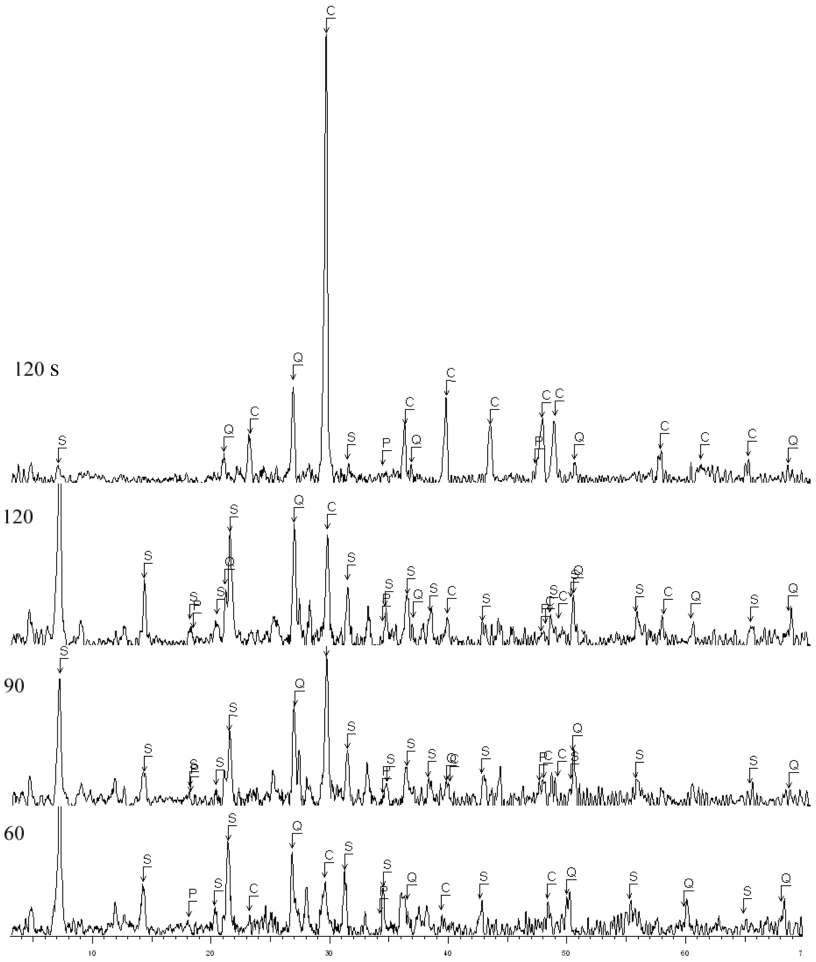


Figure 3.26 XRD traces of the mortar cubes RM-MC-Y (external surface) at 60, 90 and 120 days (from bottom to top) of curing time. 120 s denotes the XRD trace of mortar cube left on site for 120 days. C: Calcite, Q: Quartz, P: Portlandite, S: Stratlingite

The same trend could be observed for the XRD traces of the inner parts of the cubes but it was observed that calcite peak was less intense in the inner parts of the cube although stratlingite peaks kept their intensity at the inside and outside (Fig 3.27). This can be explained by the fact that for the carbonation to proceed, atmospheric CO_2 is essential which is always available on the surface of the cubes. But the diffusion of the CO_2 to the core of the cubes limits the carbonation process thus leading to slower carbonation. On the other hand pozzolanic reactions can proceed on the surface and at the inside of the cubes if there is sufficient amount of water provided by the high relative humidity or wetting without the need for atmospheric exposure.

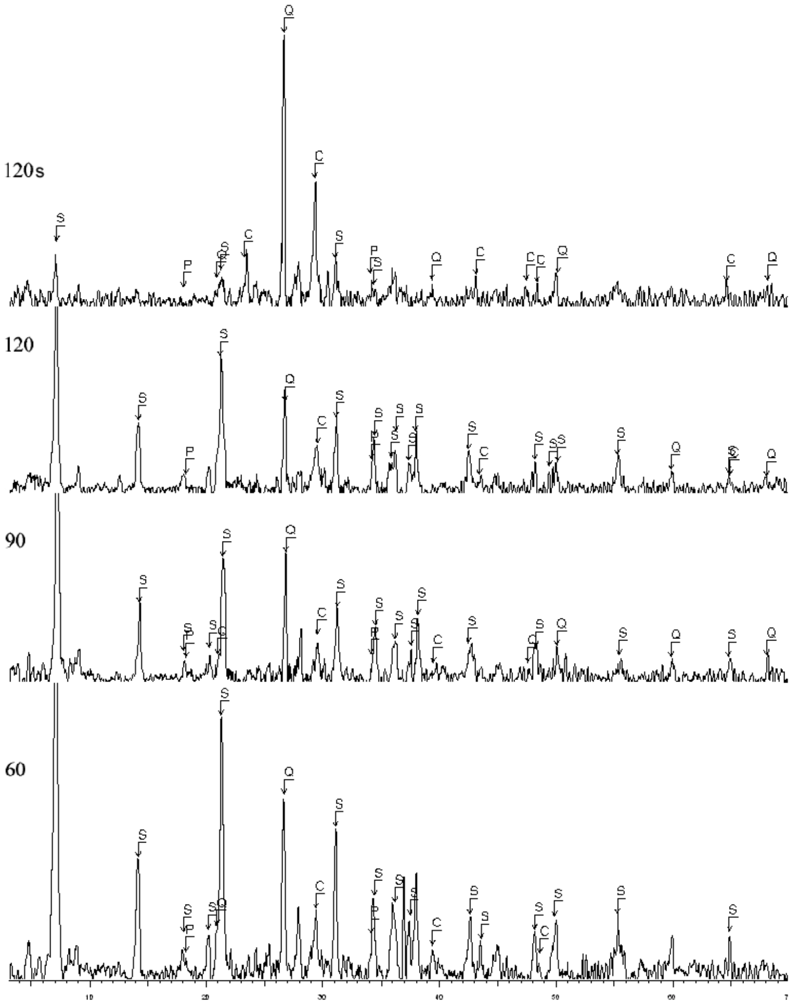


Figure 3.27 XRD traces of mortar cubes RM-MC-Y (internal surface) after 60, 90 and 120 days (from bottom to top) of curing time. 120 s denotes the XRD trace of mortar cube left on site for 120 days. C: Calcite, Q: Quartz, P: Portlandite, S: Stratlingite

The XRD traces of the external surfaces of mortar cubes, RM-MC-Z, are shown on figure 3.28. When metakaolin was used in relatively low proportions with respect to lime, the intensity of the stratlingite peaks were observed to decrease.

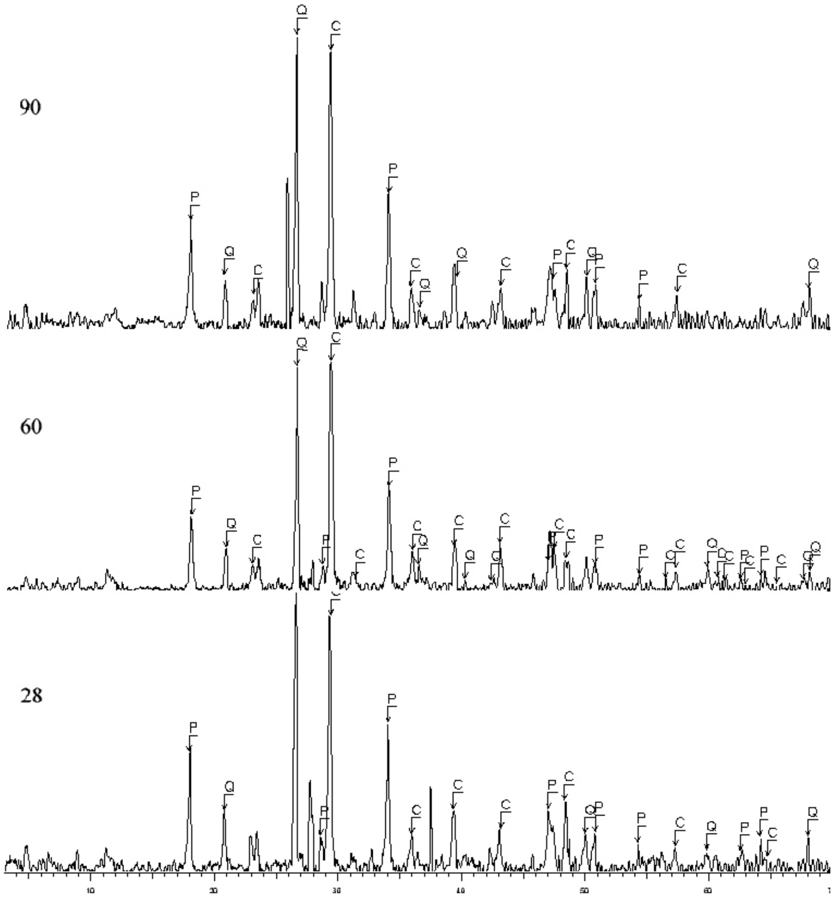


Figure 3.28 XRD traces of the mortar cubes RM-MC-Z (external surface) after 28, 60 and 90 days of curing time. C: Calcite, Q: Quartz, P: Portlandite

CHAPTER 4

DISCUSSION AND CONCLUSIONS

Experimental results of this study were discussed under the following titles; general characteristics of historic mortars, characteristics of repair mortars, progress of carbonation and pozzolanic reactions.

Characteristics of historic lime mortars

Analyses of historic mortar samples were expected to reveal the information about the relationship between their raw materials and performance characteristics which would be useful for the preparation of repair mortars.

Raw material characteristics such as the nature of binder, aggregates and pozzolanic materials of historic mortars were investigated by the determination of acid soluble/insoluble parts, particle size distribution of aggregates, pozzolanic activity tests, thin section analyses by optical microscopy, SEM analyses coupled with EDX and XRD analyses.

Historic mortars investigated gave important information about the characteristics of a durable mortar that was used for constructing limestone rubble stone masonry of Kahta Castle. Bulk densities of the historic mortars were between 1.65-1.72 g/cm3, with an average effective porosity value of 35%. Those values were in agreement with the results of historic stone masonry mortars in literature (Tuncoku 2001).

Water vapour permeability of Kahta Castle mortars was high according to the standard TS EN 1062, 7783.

The average IF value of Kahta Castle mortars were 6.7 cm^3/cm^2d showing that they were not water impermeable according to TS EN 1304 which classified a layer as a second class water impermeable layer if its IF was less than 0.9 cm^3/cm^2d.

The compressive strength of historic mortars (estimated by point load tests) was in the range of 6.3-8.4 MPa and modulus of elasticity 5010-5872 MPa. The results were in the range of the results of previous research on historical mortars from several stone masonry structures in Anatolia (Tuncoku 2001).

The analyses of acid soluble/insoluble parts of historical mortars showed that 37% of the mortar mass was acid soluble, revealing the fact that the binder could be at most 63%. This showed that a high percentage of lime was used during the preparation of those mortars. But it should also be mentioned that in the thin section examination of the historic mortars acid soluble aggregates such as limestone were encountered. Thus actual value of the binder should be lower than the indicated percentage.

Particle size distribution of the acid insoluble part of the historic mortars showed that more than 50% of the acid insoluble aggregates were consisted of particles with sizes larger than 1 mm and still larger ones up to 4mm size (Fig 3.14).

Pozzolanic activity tests showed that acid insoluble parts smaller than 125 μ had high pozzolanity (Table 3.5) showing that those lime mortars were prepared by using aggregates of which the finest aggregates had pozzolanic characteristics. It was possible that those pozzolanic fine aggregates were added to the mortar mixtures. Weight percentage of fine aggregates in the Kahta Castle mortars smaller than 250 micron was estimated to be around 13%.

Thin section analyses showed that most of the aggregates in the river sand which was used in some sets of mortars in this study were mineralogically similar to the aggregates of Kahta Castle mortars. Thus the aggregates of historic mortars from Kahta Castle were likely from the same local river (Cendere river). However, the presence of some different aggregates showed that they were some minor variations in the sand sized sediments of that river.

Examination of the white lumps in the historic mortar matrix by SEM-EDX revealed the fact that they were pure calcium carbonates, carbonated from fat lime that were unmixed with the fine aggregates during the preparation of the mortars. That result indicated that fat lime was used as the binder in the historic lime mortars studied.

Characteristics of repair mortars

Bulk density and effective porosity

Bulk densities of the prepared pozzolanic lime mortars having lime:metakaolin:aggregate ratio of 1:0.5:2 varied between 1.34-1.55 g/cm^3 and porosities between 37-44% at the end of 90 days of curing period. The bulk density of the mortars slightly increased and effective porosity was observed to decrease in time. As the carbonation and pozzolanic reactions have proceeded, the internal pores of the mortars were filled with carbonation and pozzolanic reaction products. Final results showed that bulk density and effective porosity of the repair mortars fell in the range of bulk density and effective porosity values of historic mortars analyzed in this study and others (Tuncoku 2001, Biscontin et al. 1993).

RM-MC-Y pozzolanic lime mortars which were prepared with a 1:1:1, lime:metakaolin:aggregate ratio were observed for their bulk density and effective porosity change during curing time in laboratory conditions (Fig 3.2). A set of those mortar cubes were left on site at Nemrut Dağ Monument for a period of 120 days for comparison with the mortars that were cured in high relative humidity chamber in the laboratory. The average bulk density of the mortar cubes that were kept in the laboratory were 1.09 g/cm^3 and the average porosity were 42% at the end of 120 days. The mortar cubes that were left on site for 120 days had a bulk density of 1.03 g/cm^3 and porosity of 53%.

The bulk density and porosity change of RM-MC-Z mortars which had a lime:metakaolin:aggregate ratio of 1:0.4:0.6 is shown in figure 3.3 from day 28 to day 90. the bulk density of the mortars at the end of 90 days were 1.1 g/cm^3 and the porosity were 54%.

Water impermeability and water vapour permeability of mortars

Mortars to be used for the repair of historic masonry were expected to have certain water impermeability and adequate water vapour permeability along with their other physical and physicomechanical properties such as good adhesion, high porosity, rather low but sufficient mechanical strength and compatible dilatation properties (Sasse et al. 1997).

There is lack of information on the water impermeability and water vapour permeability values on historic mortars. However, historic lime mortars are known to have rapid drying properties (Tuncoku 2001, Lanas et al. 2003).

i. Water impermeability

According to the standard TS EN 1304, a first class water impermeable layer should have an impermeability coefficient less than 0.6 cm^3/cm^{2}d. A second class water impermeable layer should have an impermeability coefficient less than 0.9 cm^3/cm^2d.

In the present study measured water impermeability coefficient of prepared repair lime mortars were variable (See Figure 3.2). The control mortar samples having no pozzolanic additives with a thickness of 2.5 cm had no water impermeability. However, pozzolanic lime mortars prepared with added fly ash, RM-FS-X, with a thickness of 2.5 cm was a first class water impermeable layer, The mortars prepared with metakaolin and brick powder however, could not reach the criteria for a second class water impermeable layer, but still had much lower water impermeability compared with the control samples without any pozzolanic additives (Fig 3.5).

ii. Water vapour permeability

Water vapour permeability is an important characteristic of lime mortars avoiding damage in the historic masonries caused by condensation. Lime mortars generally have considerable high water vapour permeability allowing the transmittance of water vapour from inside the building to the outside thus avoiding the retention of humidity in the material which could otherwise cause salt efflorescence and related problems.

Results of water vapour permeability tests performed on the repair mortars are shown in Figure 3.4. SD values of the pozzolanic lime mortars were in the range of 0.109-0.128 compared with SD value of 0.059 of control samples when the thickness of the mortars were about 2.5 cm. μ values varied between 4.819-5.458. Use of pozzolanic materials decreased the water vapour permeability slightly. Mortars prepared with metakaolin were observed to have the highest SD and μ at the end of 90 days. Control sample without any pozzolanic additive had the lowest SD and μ values thus had the highest water vapour permeability. All pozzolanic lime mortars had high water vapour permeability according to the classification denoted in the standard TS EN 1062, 7783 (Table 3.2) which is a desirable property for repair mortars.

Hydric dilatation

Control samples without any pozzolanic additive had unmeasurable point load strength in their wet state that their strength was 0, because of their disintegration when saturated with water. When the samples were saturated with water they tended to disintegrate leading to negative values for dilatation. The lowest hydric dilatation values were observed for repair mortars prepared with brick powder followed by mortars with added fly ash and metakaolin (Figure 3.6).

Shrinkage

Shrinkage during setting was also another important parameter to be followed for repair mortars. Certain shrinkage was expected in repair mortars because of the water loss during the curing period. The decrease in that parameter would favour the bonding of the mortar with the material they were used with.

The shrinkage percentages of mortar cubes at the end of 90 days (Table 3.3) showed that use of pozzolanic materials decreased shrinkage compared with the non pozzolanic control mortars. The least shrinkage was observed with mortars prepared with metakaolin and fly ash being 4.5% for both. That fact could be attributed to the high water retention capacities of the pozzolanic materials causing the water to evaporate slowly during the course of setting, thus leaving time for the carbonation and pozzolanic reactions to better proceed.

Physicomechanical properties

Use of pozzolans increased the Emod of control mortars 1.2, 1.4 and 1.8 fold for metakaolin, brick powder and fly ash added mortars respectively in comparison with control mortars (Fig 3.7). Modulus of elasticity of mortars prepared with fly ash were in the range of Kahta Castle mortars with a value of 4759 MPa.

Use of pozzolanic materials had increased the compressive strength of mortars in all mortars. Mortars prepared with fly ash had the highest compressive strength with a value of 10.2 MPa at the end of 90 days, exceeding the compressive strength of Kahta Castle mortars studied which had an average compressive strength of 7.4 MPa. Mortars prepared with metakaolin with a 1:0.5:2 binder:pozzolan:aggregate ratio almost reached the strength of Kahta Castle mortars with a value of 6.4 MPa. The durability values, defined as the wet to dry strength ratio of repair mortars prepared with metakaolin and brick powder with a binder:pozzolan:aggregate 1:0.5:2 was in the very good range, mortars according to Winkler classification (Winkler, 1986). Durability value of mortars prepared with fly ash were in the excellent category.

Progress of carbonation and pozzolanic reactions

The carbonation and pozzolanic reactions were followed by determining the unreacted $Ca(OH)_2$ by volumetric titration, XRD analyses and SEM-EDX analyses.

Free $Ca(OH)_2$ percent which showed the extend of carbonation and pozzolanic reactions were the least for the repair mortars prepared with metakaolin at the end of 28 days showing that most of it was consumed in 28 days in comparison to other pozzolanic repair mortars. At the end of 90 days, the same trend continued. Free $Ca(OH)_2$ was highest in the control samples at the end of first 14 days which could be attributed to the slow progress of carbonation. Free

$Ca(OH)_2$ percentage decreased through the end of 90 days but never reached the low values of mortars prepared with pozzolanic additives. It could be concluded that when pozzolans were used in the mixtures, it consumed $Ca(OH)_2$ during pozzolanic reactions along with carbonation leading to decreased free $Ca(OH)_2$ in mortars. The percentage of free $Ca(OH)_2$ was always higher at the inside of the cubes than at the surface because atmospheric CO_2 which was essential for the carbonation reaction to proceed was readily available at the surface of the mortar cubes. In the beginning of the setting period because the mortar was still saturated with water and the diffusion of CO_2 in water was much slower than in air, carbonation reaction was fully retarded. As the setting continued, the water slowly evaporated but as the carbonation and pozzolanic reactions proceeded, porosity of the mortars gradually decreased and thus making the diffusion of atmospheric CO_2 into the mortar more difficult. Results of free $Ca(OH)_2$ tests and XRD analyses showed that there was still unreacted $Ca(OH)_2$ in the mortar cubes even at the end of 90 days. Those results indicated that the reactions would still proceed in time if water is available.

Consumption of the $Ca(OH)_2$ and formation of $CaCO_3$ can also be followed in the XRD traces of mortars. In the XRD traces of mortars with added metakaolin, pozzolanic reaction products could be clearly identified as stratlingite peaks which showed steady increase in their intensity through time and gradual formation of calcite (Fig 3.23, 3.26, 3.27). In open air conditions, stratlingite formation was at minimum and carbonation was prominent. That might be due to the wetting drying cycles in the outdoor environment favouring carbonation over pozzolanic reactions. Development of a calcite and silica-alumina network are the characteristics of the cured binder in the pozzolanic lime mortars (Dixon and Weed 1989).

SEM analyses of the mortars prepared with added metakaolin showed the formation of the typical needle like crystals of CASH in the mortar matrix showing that pozzolanic reaction products were effectively produced in the in the binder matrix.. That observation was confirmed by the results of EDX analyses (Fig 3.19, 3.20)

By the result of the pozzolanic activity tests and the analyses of the final mineralogical and microstructural properties of mortars, it was concluded that highly active metakaolin was produced in the laboratory.

Conclusion

Characterization of historic masonry mortars is the crucial step to be completed before the design of repair mortars for the interventions to the historic masonry.

A systematic approach should be followed for the characterization of historic mortars with respect to their repair. Specific functions attributed to the mortar should be examined. Physical, mechanical and chemical compatibility of repair mortars with the authentic ones are important aspects to be considered.

Final characteristics of the designed repair mortars should be examined for their physical and physicomechanical and microstructural properties in comparison with the historic mortars. For lime mortars, formation of the final physical and physicomechanical properties take more than 28 days. 60 to 90 days of curing period would give better information about the final properties of repair mortars.

Historic mortars investigated in this study showed that historic lime mortars used for the construction of the of Kahta Castle have low bulk density (1.69 g/cm^3) and high effective porosity (35%) in agreement with previous studies. The average compressive strength of mortars were 7.4 MPa. Considering the fact that the structure still stands, the relatively low mechanical strength of mortars, compared with the contemporary cement mortars, was sufficient for historic limestone masonry. Historic mortars studied had high water vapour permeability but their water impermeability characteristics were low.

Use of fat lime in historic mortars of Kahta Castle was determined with a high binder to aggregate ratio (up to 63%). Investigation of the fine aggregates showed that they had high pozzolanicity. Comparison of the aggregates of Kahta Castle mortars with the Cendere river sand by thin section analyses indicated the use of Cendere river sand in the preparation of mortars of Kahta Castle is highly probable. Particle size distribution of the acid insoluble part showed that more than 50% of the acid insoluble aggregates were consisted of particles with sizes larger than 1 mm and still larger ones up to 4mm size.

In this study pozzolanic additives were found to be effective for the enhancement of the physical and physicomechanical properties of repair mortars. Pozzolanic materials used were observed to increase the uniaxial compressive strength and modulus of elasticity of mortars. Fly ash was the pozzolanic material that had increased the compressive strength most followed by metakaolin. Durability of the prepared repair mortars, defined by the ratio of wet to dry compressive strength were very good to excellent range according to Winkler classification. Pozzolanic additives increased the modulus of elasticity of lime mortars 1.2 to 1.8 fold compared with the control mortars without any additive.

Preparation of pozzolanic lime mortars having high water impermeability characteristics without negatively affecting water vapour permeability was achieved in this study. When used with a lime:pozzolan:aggregate ratio of 1:0.5:2 by weight, fly ash was found to give the lime mortars, a first class water impermeability according to standard TS EN 1304. If water impermeability is considered for certain repair mortars, fly ash can be used to achieve that characteristic with the suggested proportion.

Pozzolanic materials in lime mortars decreased the volume shrinkage of mortars during the curing period which is highly important, because high shrinkage affects the adhesion of the mortar to the nearby masonry unit in a negative way.

Use of pozzolanic materials decreased the free $Ca(OH)_2$ percent through the curing period. That result showed that pozzolanic reactions took place effectively in addition to the carbonation reactions in the prepared repair mortars. Results of free $Ca(OH)_2$ test revealed that there was still minor amounts of $Ca(OH)_2$ in the mortar cubes even at the end of 90 days. It can be concluded that carbonation and pozzolanic reactions would still proceed in time if mortars are wetted.

Pozzolanic activity tests, the results of XRD analyses coupled with SEM-EDX examination of mortars showed that highly reactive metakaolin was prepared in the laboratory which can be used for repair mortar preparations.

Suggestions for the preparation of repair mortars

Analyses of historic mortars is of great importance to develop an understanding of their long term performance and technologies related to their raw material characteristics and preparation techniques. The information gathered through the analyses of historic mortars should be a starting point for the development of compatible and durable historic masonry repair mortars.

For the design of repair mortars several aspects should be taken into account to ensure that final mortar is compatible with the historic one. First and foremost the role and function of the historic mortar in the masonry element and the role of the masonry element in the building should be taken into consideration (Van Balen et al. 2005). Functional requirements of repair mortars in regard to its use in the masonry can be revealed by the examination of the following properties of historic mortars. Since it is not always possible to gather adequately sized historic mortar samples needed to perform standard tests, some modifications may be required during the test processes.

- Physicomechanical properties
    - the load bearing capacity and mechanical performance of the mortar by compressive strength and modulus of elasticity tests,
- Basic physical properties
    - bulk density and effective porosity,

- water vapour permeability, water impermeability and water absorption by capillarity which affect the water and water vapour transfer through the masonry system,
- hydric and thermal dilatation properties.

The strength of mortars should be estimated by either direct compressive strength tests or indirect uniaxial compressive strength tests by using point load strength measurements (section 2.4.2) and Emod calculations (section 2.4.1) if it is difficult to use standard sized samples. The results should be evaluated considering the deterioration state of the historical mortar sample because of its exposure to environmental factors through its lifetime. Therefore an estimation is required for the determination of the repair mortar strength considering the function and the deterioration state of the original mortar and stone (Van Balen et al. 2005).

Basic physical properties of bulk density and porosity of the repair mortars should match with those of historical mortars since those properties are directly related to most of the performance characteristics of mortar. Ensuring good match for those properties increases the probability of the repair mortar to be compatible with the original mortar. In order to develop repair mortars with predefined bulk density and effective porosity, the binder/aggregate ratio, particle size distribution of the aggregates, water content of the mortar mixtures, and addition of pozzolanic additives should be considered.

Water impermeability and water vapour permeability characteristics of historic mortars and repair mortars should be investigated to make sure that the repair mortar does not pose any threat to the continuity of the masonry system in terms of those parameters. Failure to match these characteristics in repair mortars may eventually cause serious dampness problems leading to an unsuccessful repair.

Compatibility between historic mortar and repair mortar in terms of hydric and thermal dilatation characteristics is important since effective bonding of the repair mortar and historic mortar is ensured when both have similar hydric and thermal dilatation characteristics and acts against changes in atmospheric conditions together. Otherwise detachments at the bonding interface between the repair mortar and the original mortar is inevitable.

Determination of raw material properties which are directly related to the characteristics of mortars, should be performed through a series of systematic analyses, results of which would be utilized as a guide for the design of the repair mortar mixtures.

Investigation of the raw material characteristics involve the determination of nature of binder and its hydraulicity, nature of aggregates, the relative ratio of binder and aggregates and the particle size distribution of aggregates.

Composition of the mortars should be investigated by the use of chemical and mineralogical analyses. Determination of the binder aggregate ratio by determining the acid soluble and insoluble parts and the grading of the aggregates by sieve analyses are crucial. Mineralogical examination of the aggregates through thin section analyses is important to reveal the type and nature of aggregates. Thin section analyses coupled with image processing also gives information about the binder aggregate ratio and particle size distribution of the acid soluble aggregates and therefore can be used to back up the results of acid soluble/insoluble parts tests and particle size distribution by sieve analyses. Pozzolanic activity measurements of the finest aggregates are of special importance regarding the raw material characteristics of mortars. Identification of mineralogical composition of the pozzolanic additives would give valuable information about the percentage and quality of the pozzolanic additives to be added to repair mortars. Although those analyses would only indicate the activity of remaining pozzolans due to acid solubility of previous pozzolanic reaction products, the data collected would be useful to discover local technologies and raw material sources in relation to pozzolanic materials.

The development of compatible repair mortars to be used in successful interventions can only be accomplished by performing those investigations on historic mortars before the design process. To evaluate the compatibility, the physical and physicomechanical characterization should be performed on the prepared repair mortars. Curing of repair mortars and formation of their final physical and physicomechanical properties take more than 28 days which is the standard curing time for performing tests on contemporary cement mortars. Thus 60 to 90 days of curing period would give better information about the final properties of repair mortars for their evaluation.

Those parameters explained above give important information that would be useful for the design and performance analyses of repair mortars. Those tests are essential to evaluate the compatibility and durability of repair mortars.

Further studies

Investigation of the mechanisms of pozzolanic reactions and carbonation separately and together would give insight to the setting behaviour of mortars, so need to be further studied. Stability of the pozzolanic reaction products and their conversion products in prolonged time periods need to be studied to better understand historic lime mortars with pozzolanic additives. Methods for the colouring of repair mortars should be investigated in order to match the repair mortars with the original mortars aesthetically.

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