UDK 666.971.3:693.6:94(560Anaia Kadikalesi) ISSN 1580-2949
Original scientific article/Izvirni znanstveni članek MTAEC9, 56(5)461(2022)

CHARACTERISTICS OF BYZANTINE-PERIOD LIME MORTARS AND PLASTERS FROM THE ANAIA CHURCH (KADIKALESI)

ZNAČILNOSTI APNENIH MALT IN OMETOV S CERKVE ANAIA IZ BIZANTINSKEGA OBDOBJA

Tuğçe Işık*, Elif Uğurlu Sağın

İzmir Institute of Technology, Faculty of Architecture, Department of Conservation and Restoration of Cultural Heritage, Urla, Izmir, Turkey

Prejem rokopisa – received: 2022-03-15; sprejem za objavo – accepted for publication: 2022-06-10

doi:10.17222/mit.2022.524

In this study, Byzantine-period lime mortars and plasters used in the Anaia Church in Kuşadası- Aydın were examined in order to determine their characteristics and investigate the continuity of the lime mortar technology through centuries in the Anaia Church. The results will also contribute to future conservation studies at the site. Basic physical properties, raw-material compositions and hydraulic properties of lime mortars and plasters; mineralogical and chemical compositions, microstructural properties of binders, aggregates and limes; and pozzolanic activities of aggregates were determined using RILEM test methods, XRD, SEM-EDS and TGA. Mortar samples were comprised of natural aggregates whereas lime plasters were made of brick aggregates. Analyses revealed that plasters were slightly less dense and more porous than mortars due to the porous structure of the brick aggregates. All mortars and plasters were hydraulic due to the use of highly reactive pozzolanic aggregates. The basic physical properties, raw-material compositions, mineralogical and chemical compositions of mortars and plasters were found to be similar throughout the construction periods spread over different centuries. These similarities revealed the conscious knowledge of the lime mortar technology during the Byzantine period in Western Anatolia.

Keywords: Byzantine period, hydraulic lime mortar, pozzolan, characterization

Predstavljena študija preučuje apnene malte in omete s cerkve Anaia v kraju Kuşadası- Aydın, ki so iz bizantinskega obdobja. Namen študije je določitev lastnosti the materialov in preučevanje tehnologije apnenih malt na cerkvi skozi stoletja. Izsledki študije bodo prispevali h konservatorskim pristopom na cerkvi v bodoče. Osnovne fizikalne lastnosti, surovinsko sestavo in hidravlične lastnosti apnenih malt in ometov; mineraloško in kemijsko sestavo, mikrostrukturne lastnosti veziv, agregatov in vrst apna ter pucolanske aktivnosti agregatov; smo določili z RILEM-ovi testnimi metodami, XRD, SEM-EDS in TGA. Maltni vzorci so vsebovali naravne agregate, ometi pa so bili pripravljeni z opečnimi agregati. Z analizami smo ugotovili, da imajo ometi manjšo gostoto in so bolj porozni kot malte. To lahko pripišemo porozni strukturi opečnih agregatov. Vsi ometi in malte vsebujejo hidravlične produkte, zaradi visoko reaktivnih pucolanskih agregatov. Osnovne fizikalne lastnosti, sestave osnovnih materialov, mineraloške in kemijske sestave malt in ometov se skozi stoletja niso spreminjale, kar nakazuje na ohranjanje znanj o tehnologiji apnenih malt med bizantinskim obdobjem v Zahodni Anatoliji.

Ključne besede: bizantinsko obdobje, hidravlična apnena malta, pucolan, karakterizacija

1 INTRODUCTION

Historical lime mortars and plasters were produced using non-hydraulic lime and natural or artificial pozzolanic aggregates. Amorphous silica and alumina in the structures of pozzolans react with lime in the presence of water, and calcium silicate hydrate (CSH) and calcium aluminate hydrates (CAH) that provide hydraulic properties to mortars and plasters are formed as the result of this reaction.[1,2] Hydraulic, mechanical, and microstructural properties of lime mortars produced using pozzolanic aggregates had been appreciated by different civilizations like Romans, Byzantines and Ottomans. Lime mortars provided stability and durability especially to water-related structures throughout centuries until the invention of modern cement.[3]

It is known that lime had been produced in the kilns situated close to the raw material sources, and lime mortars had been manufactured close to the building sites by local craftsmen.[4] Therefore, they can be accepted as the characteristics of the region and the period, in which they were produced. Characterization of lime mortars and plasters and determination of the chemical, mineralogical and microstructural properties of their raw materials will provide historical information about their production as well as a better understanding of the structures applied.

This study aims to determine the physical, mineralogical and hydraulic characteristics of Byzantine-period lime mortars and plasters from different construction periods of the Anaia Church (Kadıkalesi) in Western Anatolia (Turkey) in order to investigate the continuity of the lime mortar technology and raw material use throughout the centuries. The results will also contribute to future conservation studies at the site.

The Anaia Church surrounded by the Kadıkalesi fortification walls was built on a prehistoric mound in the 5–6th centuries.[5,6] It had served as the bishopric of the Ephesus Metropolis between the 5–13th centuries and became the archbishopric in the 13th century.[5,7–9] The Anaia

*Corresponding author's e-mail:
tugceisik@iyte.edu.tr (Tuğçe Işık)

Church is of great importance as it exhibits an architectural and symbolic value comparable to the monumental structures from Constantinople (İstanbul), the Byzantine capital city.

Three construction periods were determined in the Anaia Church, taking into consideration the spatial organization, construction techniques, materials and architectural elements such as ambo and synthronon (**Figure 1**).[6] The first construction period (Early Byzantine in the $5–6^{th}$ centuries) with three naves, a naos, a narthex and atrium spaces covered with a wooden roof was considered.[6]

There had been three major earthquakes that severely damaged the Church in 1039, 1040 and 1056 with the intensities of grades VII and VIII according to the MSK-64 intensity scale.[10] Following these earthquakes, the damaged north and south facade walls of the naos and narthex were rebuilt and strengthened with buttresses during the second construction period between the $11–13^{th}$ centuries (the Middle Byzantine period).[6,11] The Middle Byzantine period additions can be distinguished due to the differences in the wall bonding techniques, recessed brick technique and the separations between the wall joints. The third construction period was determined to be between the 13^{th} and 14^{th} centuries (the Late Byzantine period) due to sharp wall separations and different bonding techniques. In this period, the Church was extended with the baptistery, cisterns and outer narthex. Besides, the naos walls and buttresses, and inner narthex buttresses were built to strengthen the Church structure.[6,11]

2 EXPERIMENTAL PART

In this study, 9 lime mortar (M) and 5 lime plaster (P) samples were taken from the baptistery (Ba), cistern I (C), cistern II (C), naos (N), outer narthex (O) and substructure (S) of the Anaia Church which were dated to different construction periods (**Figure 1**). The sampling was carried out on the undeteriorated parts of the Church.

Experimental studies were carried out to determine the basic physical properties, raw material compositions and hydraulic properties of the lime mortars and plasters; mineralogical and chemical compositions, microstructural properties of binders, aggregates and limes; as well as pozzolanic activities of the aggregates via the RILEM test methods, XRD, SEM-EDS and TGA.

The basic physical properties of the lime mortars and plasters were determined with RILEM tests that described their bulk density and porosity values.[12] The raw material compositions defined by the lime/aggregate ratio and the particle size distributions of the aggregates were determined by dissolving carbonated lime ($CaCO_3$) with a diluted hydraulic acid (5 %), washing, drying and sieving the aggregates. The mineralogical compositions of the finely ground aggregates, binders and limes of less than 53 μm were detected using X-ray diffraction (XRD). XRD analyses were done using a Philips X-Pert Pro X-ray diffractometer with CuK_{α} radiation, operating at 40 kV and 40 mA in a range of 5–60° with a scan speed of 0.08 °/s. The chemical compositions of the aggregates, binders and limes were determined via a scanning electron microscope (SEM) coupled with an X-ray energy dispersive system (EDS). SEM-EDS analyses were carried out with a Philips XL 30S FEG on pellets obtained from powder samples pressed with a pressure of 980.665 MPa (10 t/cm^2). Semi-quantitative results for the chemical compositions were obtained by averaging the data derived from three distinct areas of the samples following the k-ratio protocol. The data were collected without using a standard sample. The results were also

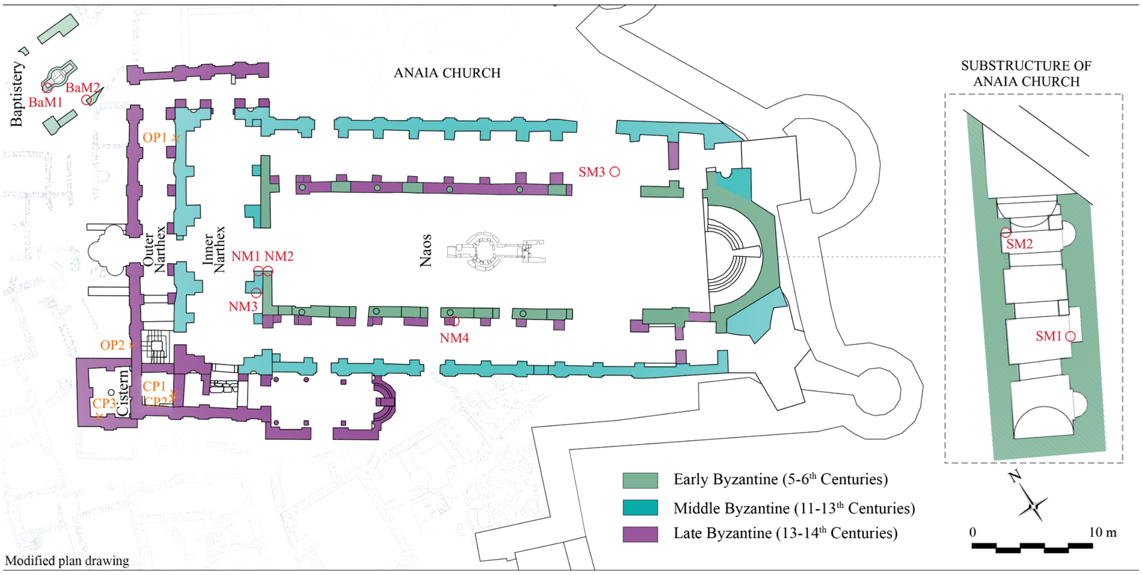

Figure 1: Plan showing the construction periods of the Anaia Church and sample locations

used to calculate the hydraulic HI (Equation (1)) and cementation CI (Equation (2)) indices to identify the hydraulicity of the lime lumps.[13,14]

$$HI = \frac{(\%Al_2O_3 + \%Fe_2O_3 + \%SiO_2)}{(\%CaO + \%MgO)} \quad (1)$$

$$CI = \frac{(2.8 \cdot \%SiO_2 + 1.1 \cdot \%Al_2O_3 + 0.7 \cdot \%Fe_2O_3)}{(\%CaO + 1.4 \cdot \%MgO)} \quad (2)$$

The pozzolanic activities of the aggregates were determined by measuring the differences in electrical conductivity taken before and after the addition of fine aggregates (< 53 µm) into the saturated calcium hydroxide solution ($Ca(OH)_2$).[15] Electrical-conductivity differences higher than 40 mS/m indicate that aggregates are pozzolan, while a value of 120 mS/m indicates that aggregates have good pozzolanicity.[15] Pozzolanic activities were also evaluated with the chemical compositions using the ASTM C618-03 standard. According to this standard, the SiO_2 + Al_2O_3 + Fe_2O_3 content of pozzolanic materials should be above 70 %.[19]

The hydraulic properties of mortars and plasters were determined by measuring the weight losses due to the loss of chemically bound water (H_2O) of hydraulic products between 200–600 °C (H_2O) and the release of carbon dioxide (CO_2) during the decomposition of $CaCO_3$ between 600–900 °C (CO_2) via TGA.[16] Accordingly, a CO_2/H_2O ratio lower than 10 indicates the hydraulic character of mortar or plaster.

Microstructural properties and morphologies of the mortars and plasters were specified with a scanning electron microscope (SEM) coupled with an X-ray energy dispersive system (EDS) (Philips XL 30S FEG). Analyses were carried out on polished and broken surfaces of lime mortars using the secondary electron (SE) and backscattered electron (BSE) modes at different magnifications in order to examine the general microstructure of the mortars, properties of pozzolan-binder interfaces and microstructural characteristics of pozzolans.

3 RESULTS AND DISCUSSION

3.1 Basic physical properties and raw-material compositions of lime mortars and plasters

Macroscopic investigations revealed that all the lime mortars consisted of natural aggregates and had a greyish color, whereas the lime plasters were composed of brick aggregates and had a pinkish color. All the samples were sound with a stiff and compact appearance.

The lime mortars with natural aggregates had higher density and lower porosity of 1.54–1.73 g/cm^3 and 31–37 %, respectively (**Table 1**). However, the lime plasters with brick aggregates were less dense and more porous with values of 1.30–1.42 g/cm^3 and 43–47 %, respectively (**Table 1**). These differences may be explained with the porous structure of brick aggregates.[17,18] It is known that the porous structure of brick aggregates enhances the resistance of plasters to deterioration, making them ideal materials, especially for water-related structures.[17]

Lime/aggregate ratios by weight were found to be between 1/3–4/3 for the plasters, 1/2–1/1 for the Early Byzantine lime mortars, and between 4/3–5/3 for the Middle and Late Byzantine buttress mortars (**Table 1**). These differences might be due to either the use of lime as the binder or the existence of calcareous based particles in aggregates. Previous studies showed that a higher amount of the binder provides better bonding between the structural components and a greater mechanical strength in lime mortars.[20–24] The buttresses were thought to be added to the Anaia Church after the earthquakes that took place in the Middle and Late Byzantine periods.[6] The mortars used in the construction of the buttresses may have been produced with a higher lime/aggregate ratio to provide a higher strength to resist future earthquakes.

The particle-size distribution of aggregates is another important feature in defining the raw-material compositions of lime mortars and plasters since it is known that

Table 1: Physical properties and raw-material compositions of the lime mortars and plasters

Period	Sample	Location	Function	Aggregate type	Density (g/cm^3)	Porosity (%)	Lime/aggregate (by weight)
Early Byzantine	BaM1	Baptistery wall	Mortar	Natural	1.72	31	0.78
	BaM2	Baptistery wall	Mortar	Natural	1.63	36	1.10
	NM2	Naos wall	Mortar	Natural	1.66	34	0.86
	SM1	Substructure arch	Mortar	Natural	1.62	37	1.14
	SM2	Substructure buttress	Mortar	Natural	1.72	32	0.51
	SM3	Substructure vault	Mortar	Natural	1.58	37	1.14
Middle Byzantine	NM1	Naos buttress	Mortar	Natural	1.67	35	1.44
	NM3	Naos buttress	Mortar	Natural	1.73	31	1.66
	OP1	Outer narthex wall	Plaster	Brick	1.31	43	1.15
Late Byzantine	OP2	Outer narthex wall	Plaster	Brick	1.42	44	1.04
	CP1	Cistern I wall	Plaster	Brick	1.34	48	0.72
	CP2	Cistern I wall	Plaster	Brick	1.36	44	1.38
	CP3	Cistern II wall	Plaster	Brick	1.30	46	0.37
	NM4	Naos buttress	Mortar	Natural	1.54	34	1.36

the particle sizes of aggregates effect the physical properties, durability and mechanical strength of mortars. The natural aggregates of Kadıkalesi had higher amounts of aggregates with sizes of > 1180 µm (4–37 %), and also aggregates of 1180–500 µm (8–21 %), 500–250 µm (5–32 %), 250–125 µm (3–14 %), 125–53 µm (2–7 %) by weight, and lower amounts of aggregates of < 53 µm (0.5–2 %) by weight. Within the distribution of brick aggregates, the weight percentages of the aggregates of the sizes > 1180 µm (10–19 %), 500–250 µm (9–17 %), 1180–500 µm (4–12 %) were lower; and the weight percentages of the aggregates with the sizes of 250–125 µm (5–12 %), 125–53 µm (6–12 %) and < 53 µm (0.5–5 %) were higher when compared with the distribution of natural aggregates. Consequently, the aggregates had a wide range of particle sizes, enhancing the mechanical strength of the mortars.

3.2 Characteristics of the lime used in the production of mortars and plasters

White nodules of a few millimeters in the lime mortars and plasters were considered as "lime lumps", which might have occurred during the mixing of lime and aggregate.[25] Since lime lumps were considered to represent lime, their chemical and mineralogical compositions were accepted to be the same as those of the raw material.[25–27] In the XRD patterns of the lime lumps from all the periods, only sharp calcite peaks were identified (**Figure 2c**). The SEM-EDS analysis indicated that lime lumps mainly consisted of large amounts of CaO (97–98 %) and smaller amounts of SiO_2 (0.6–1.2 %), MgO (0.6–0.9 %), Na_2O (0–0.1 %), Al_2O_3 (0.4–0.6 %), K_2O (0–0.2 %) and were without TiO_2 or Fe_2O_3.

Hydraulic and cementation indices were calculated using the chemical compositions according to the Boynton formula. Hydraulic-index (HI) values lower than 0.1, and cementation-index (CI) values lower than 0.3 demonstrate a non-hydraulic character of lime. HIs and CIs of the lime lumps of the Anaia Church mortars were found to be between 0.01–0.02 and 0.03–0.04, respectively.[13,14] The mineralogical and chemical compositions and HI and CI values showed that the lime used in the production is non-hydraulic and fat.[13,14] Micritic calcite crystals smaller than 5 µm were observed in SEM images (**Figures 2a** and **2b**). This may indicate that the lime had been used after a long aging.[28]

3.3 Characteristics of the natural and brick aggregates used in mortars and plasters

The pozzolanic activities of the aggregates were determined by following the electrical conductivity differences in the saturated calcium hydroxide solution before and after the addition of fine samples (< 53 µm).[15] Electrical conductivity differences were found to be between 150–800 mS/m for the natural aggregates, and between 570–709 mS/m for the brick aggregates (**Table 2**). The

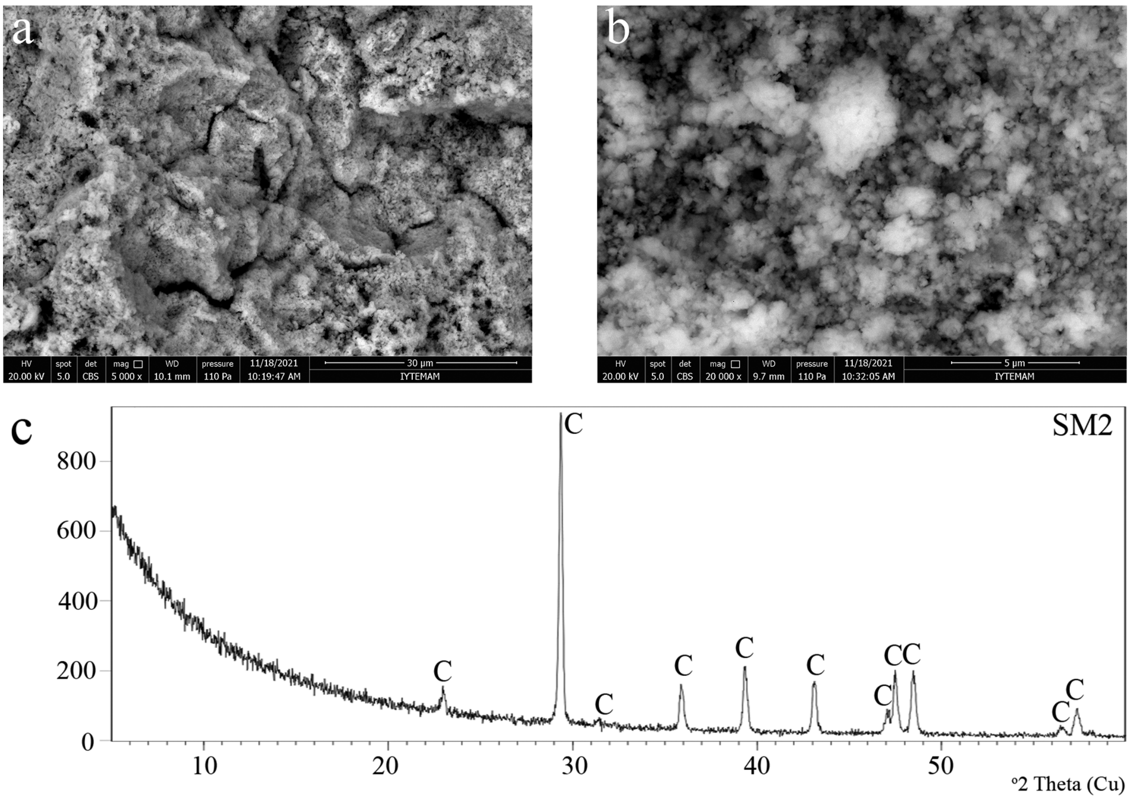

Figure 2: Typical lime lump (SM2 sample) consisting of micritic calcite crystals: a) SEM 5000×, b) SEM 20000×, c) XRD pattern (C: calcite 86-2334)

Table 2: Chemical and mineralogical compositions and electrical-conductivity differences (E.C.D.) of the aggregates

Period	Sample	Major oxide compositions (%)								Mineralogical compositions						Pozzolanic activity	
		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Q	A	M	C	O	H	E.C.D. (mS/m)	SiO_2+ Al_2O_3+ Fe_2O_3 (%)
Early Byzantine	BaM1	0.60 ± 0.08	2.29 ± 0.29	11.26 ± 0.72	75.77 ± 1.55	2.25 ± 0.10	1.55 ± 0.14	0.84 ± 0.05	5.44 ± 0.43	+++	++	+	+	-	-	713	92.47
	BaM2	1.86 ± 0.42	2.23 ± 0.44	12.71 ± 0.72	73.47 ± 1.70	2.77 ± 0.27	1.81 ± 0.30	0.76 ± 0.84	4.39 ± 0.75	+++	+	++	+	++	-	797	90.57
	NM2	0.62 ± 0.11	4.21 ± 0.03	16.07 ± 0.39	66.90 ± 0.24	3.20 ± 0.04	0.74 ± 0.08	1.04 ± 0.13	7.23 ± 0.23	+++	++	++	++	-	-	553	90.20
	SM1	0.66 ± 0.12	4.39 ± 0.42	15.47 ± 0.54	66.80 ± 1.08	3.19 ± 0.06	1.06 ± 0.05	0.94 ± 0.12	7.48 ± 0.45	+++	++	++	-	-	-	151	89.75
	SM2	2.34 ± 0.41	1.80 ± 0.15	16.87 ± 1.32	69.53 ± 1.20	2.83 ± 0.50	0.63 ± 0.13	0.71 ± 0.56	5.29 ± 1.02	+++	++	++	-	-	-	164	91.69
	SM3	0.63 ± 0.16	3.02 ± 0.33	12.54 ± 0.15	74.38 ± 0.65	2.79 ± 0.19	0.83 ± 0.07	0.64 ± 0.22	5.18 ± 0.11	+++	++	++	++	++	-	803	92.10
Middle Byzantine	NM1	0.78 ± 0.11	3.27 ± 0.19	14.11 ± 0.35	69.74 ± 0.67	3.40 ± 0.07	0.99 ± 0.07	1.22 ± 0.21	6.51 ± 0.65	+++	++	++	++	-	-	433	90.36
	NM3	0.80 ± 0.16	3.02 ± 0.40	13.56 ± 0.83	71.53 ± 1.18	3.11 ± 0.10	1.17 ± 0.13	1.00 ± 0.18	5.82 ± 0.17	+++	++	++	+	-	-	790	90.91
	OP1	0.99 ± 0.12	1.35 ± 0.14	13.60 ± 0.30	73.41 ± 0.66	2.89 ± 0.23	0.83 ± 0.09	0.80 ± 0.24	6.13 ± 0.23	+++	++	++	-	-	+	757	93.14
Late Byzantine	OP2	0.99 ± 0.21	2.08 ± 0.14	16.76 ± 0.13	67.20 ± 0.49	3.76 ± 0.17	1.23 ± 0.06	0.73 ± 0.41	7.26 ± 0.32	+++	++	++	-	-	+	568	91.22
	CP1	0.52 ± 0.12	2.07 ± 0.10	10.41 ± 0.27	78.15 ± 0.52	2.13 ± 0.05	2.09 ± 0.23	0.58 ± 0.10	4.04 ± 0.54	+++	++	++	-	-	+	769	92.60
	CP2	0.49 ± 0.08	2.98 ± 0.18	14.40 ± 0.13	66.12 ± 0.19	3.04 ± 0.20	4.10 ± 0.14	1.03 ± 0.06	7.83 ± 0.31	+++	++	++	-	-	-	785	88.35
	CP3	0.47 ± 0.13	3.07 ± 0.12	12.06 ± 0.70	71.90 ± 0.53	2.60 ± 0.10	2.96 ± 0.16	0.93 ± 0.10	6.01 ± 0.38	+++	++	++	-	-	+	785	89.97
	NM4	0.37 ± 0.07	2.24 ± 0.14	15.27 ± 0.17	71.14 ± 0.39	3.27 ± 0.14	0.85 ± 0.06	1.46 ± 0.30	5.40 ± 0.55	+++	++	++	+	-	-	308	91.81

The number of pluses represents the abundance of mineral peaks. (Q: quartz, A: albite, M: muscovite, Cl: clinochlore, O: orthoclase, H: hematite)

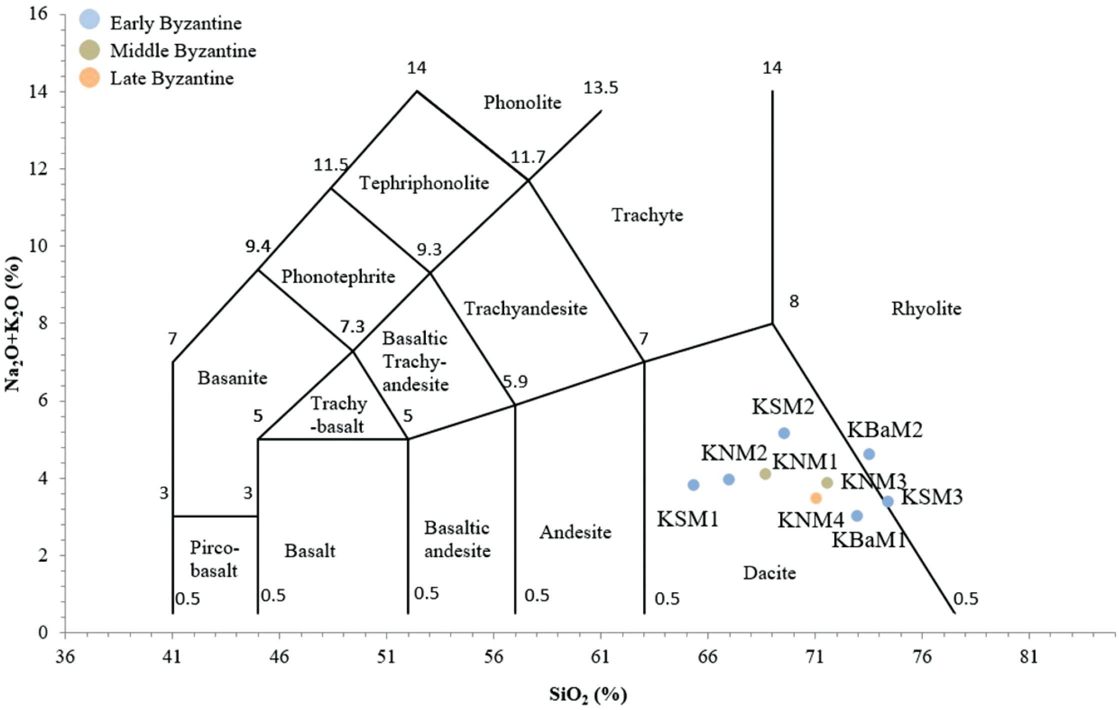

Figure 3: TAS diagram showing geochemical origins of the fine natural aggregates

results greater than 120 mS/m revealed that both the natural and brick aggregates used in the mortars and plasters from all periods exhibited highly reactive pozzolanic properties.[15]

SEM-EDS analyses revealed that the natural aggregates in lime mortars were mainly composed of large amounts of SiO_2 (66.8–75.8 %), moderate amounts of Al_2O_3 (11.3–16.9 %) and smaller amounts of Fe_2O_3 (4.4–7.4 %), MgO (1.8–4.4 %), K_2O (2.2–3.4 %), Na_2O (0.4–2.3 %), CaO (0.6–1.8 %) and TiO_2 (0.6–1.5 %) (**Table 2**). The SiO_2 + Al_2O_3 + Fe_2O_3 content of the natural aggregates was in a range of 89.75–92.47, indicating their pozzolanic property.[19]

Possible geochemical classes of fine natural aggregates (< 53 μm) were evaluated using the total alkali-silica (TAS) diagram according to the major oxide compositions.[29] According to the TAS diagram, all fine natural aggregates from the Middle and Late Byzantine period and some from the Early Byzantine periods (BaM1, NM2, SM1, SM2) were classified as the dacite group, while two of the Early Byzantine samples (BaM2, SM3) were in the rhyolite group (**Figure 3**). The fine natural aggregates from the dacite group were composed of quartz, albite, muscovite and clinochlore, while the fine natural aggregates from the rhyolite group also contained orthoclase (**Figures 4b** and **4d**), (**Table 2**).

The use of volcanic aggregates was a common practice in the ancient Hellenistic, Roman and Byzantine settlements in western Anatolia that has rich igneous rock resources.[18,30–32] Future interdisciplinary studies may provide more precise information about the provenance of natural aggregates. Determining the sources will also be necessary for the mortars to be produced for the conservation works in the future.

The chemical compositions of the brick aggregates used in the Middle and Late Byzantine lime plasters mainly consisted of large amounts of SiO_2 (66.1–78.2 %), moderate amounts of Al_2O_3 (10.4–16.8 %) and smaller amounts of Fe_2O_3 (4.0–7.8 %), MgO (1.4–3.1 %), K_2O (2.1–3.8 %), Na_2O (0.5–1.0 %), CaO (0.8–4.1 %) and TiO_2 (0.6–1.0 %) according to SEM-EDS (**Table 2**). Smaller amounts of CaO indicated that all the brick aggregates were produced from Ca-poor clay sources. The SiO_2 + Al_2O_3 + Fe_2O_3 values were found to be in a range of 88.35–93.14, indicating a pozzolanic property as determined with the electrical-conductivity analysis.[19]

The XRD analysis demonstrated that the brick aggregates were mostly comprised of quartz, albite and muscovite. Different mineral phases of the brick aggregates were used to predict their firing temperatures. At firing temperatures exceeding 900 °C, amorphous substances begin to disappear and pozzolanic activities are lost. The pres-

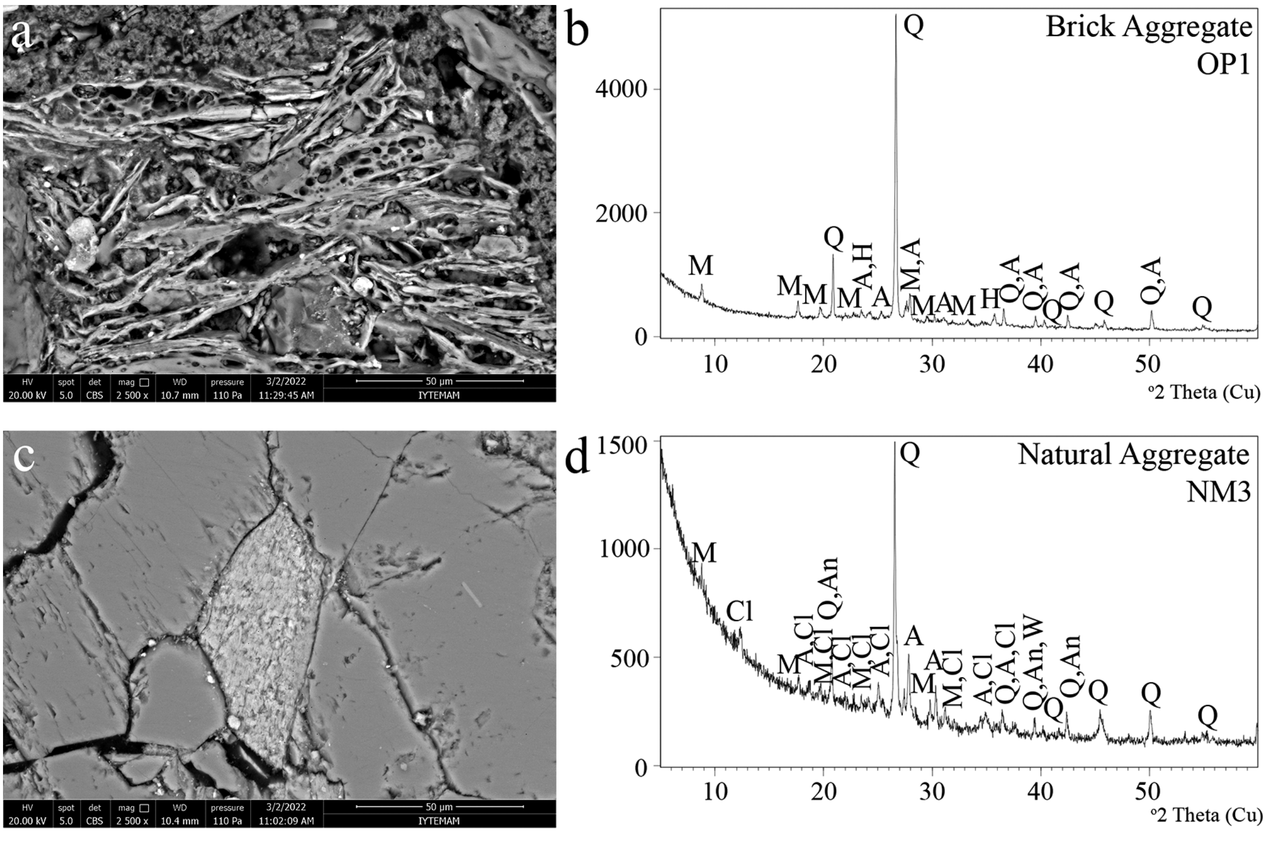

Figure 4: SEM images and XRD diffraction patterns of the aggregates: a) brick SEM 2500×, b) brick XRD, c) natural SEM 2500×, d) natural XRD (A: albite 76–1819, Cl: clinochlore 79–1270, H: hematite 87–1166, M: muscovite 84–1302, Q: quartz 85–0798)

ence of mineral phases such as mullite (≈ 1000 °C), cristobalite (≈ 1200 °C) or wollastonite (≈ 900–1050 °C) indicated high firing temperatures.[33,34] Pozzolanic properties and the absence of high-temperature minerals suggested that the firing temperature did not exceed ≈ 900 °C in all the brick aggregates.

Microstructural properties of the aggregates were determined with SEM-EDS. SEM images showed that brick aggregates had a more porous structure than natural aggregates. The microstructure of the brick aggregates also exhibited little vitrification, confirming low firing temperatures during their production. Both aggregates were comprised of amorphous particles with an irregular morphology, which can be associated with their pozzolanic properties (**Figures 4a** and **4c**). These amorphous substances could not be determined with the XRD patterns since their non-crystalline structure did not give any indicative peaks.

3.4 Characteristics of the binders of mortars and plasters

Fine mortar and plaster matrices, finer than 63 µm, consisted of small grain-sized aggregates and carbonated lime was defined as the "binder".[25,35] Binders are the parts that provide high strength and hydraulic characteristic to mortars. The SEM-EDS analysis revealed that the binders comprised of natural aggregates had a larger amount of CaO (67.0–87.2 %) and small amounts of SiO_2 (6.9–20.3 %) and Al_2O_3 (2.2–6.4 %), while the binders with brick aggregates consisted of a larger amount of CaO (36.4–64.9 %) and moderate amounts of SiO_2 (19.5–34.5 %) and Al_2O_3 (9.2–14.1 %) (**Table 3**).

In the XRD diffraction patterns of the binders with natural or brick aggregates, calcite originating from lime; and quartz, albite and muscovite originating from aggregates were determined (**Figures 5b** and **6b**), (**Table 3**). Mineralogical compositions of the binders indicated similar characteristics throughout different periods. Hydraulic products like calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH) formed as the result of the reaction between the pozzolanic aggregates and lime binder could not be detected due their amorphous structure.

Hydraulic properties of the binders were determined by calculating the percentages of weight losses between 200–600 °C and 600–900 °C, detected via TGA. The weight losses between 200–600 °C were due to structur-

Table 3: Chemical, mineralogical compositions and hydraulic properties of the binders

Period	Sample	Major oxide compositions (%)								Mineralogical compositions				Hydraulic properties
		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	C	Q	A	M	$\frac{CO_2}{H_2O}$
Early Byzantine	BaM1	0.22 ± 0.11	3.65 ± 0.36	6.18 ± 0.92	19.08 ± 1.10	1.30 ± 0.15	66.95 ± 1.04	0.35 ± 0.18	2.28 ± 0.23	+++	++	+	+	5.8
	BaM2	0.00 ± 0.13	1.41 ± 0.09	2.69 ± 0.87	7.45 ± 0.05	0.65 ± 0.15	86.47 ± 0.44	0.05 ± 0.05	1.28 ± 0.36	+++	++	+	+	9.1
	NM2	0.33 ± 0.03	2.47 ± 0.36	6.40 ± 0.08	20.25 ± 1.45	1.16 ± 0.18	67.14 ± 0.12	0.35 ± 1.98	1.90 ± 0.10	+++	++	+	+	5.2
	SM1	0.46 ± 0.21	1.95 ± 0.08	2.83 ± 0.18	9.45 ± 0.34	0.87 ± 0.09	83.54 ± 1.03	0.00 ± 0.00	0.90 ± 0.25	+++	++	+	+	8.5
	SM2	0.43 ± 0.16	2.68 ± 0.26	4.94 ± 2.18	16.12 ± 0.92	1.25 ± 0.11	72.50 ± 1.39	0.16 ± 0.17	1.92 ± 0.20	+++	++	+	+	7.2
	SM3	0.29 ± 0.16	1.91 ± 0.17	2.19 ± 0.62	6.85 ± 0.65	0.37 ± 0.18	87.24 ± 0.52	0.12 ± 0.06	1.02 ± 0.29	+++	++	+	+	8.1
Middle Byzantine	NM1	0.23 ± 0.02	1.40 ± 0.19	2.99 ± 0.19	9.69 ± 0.59	0.44 ± 0.11	84.53 ± 1.25	0.00 ± 0.00	0.72 ± 0.44	+++	++	+	+	10.0
	NM3	0.42 ± 0.20	2.01 ± 0.26	5.13 ± 0.80	18.95 ± 1.18	0.85 ± 0.15	71.51 ± 0.56	0.00 ± 0.00	1.13 ± 0.28	+++	++	+	+	8.3
	OP1	0.42 ± 0.07	6.67 ± 0.01	14.05 ± 0.18	34.51 ± 0.28	2.48 ± 0.11	36.42 ± 0.64	0.58 ± 0.16	4.87 ± 0.37	+++	++	+	+	3.4
Late Byzantine	OP2	0.61 ± 0.14	5.66 ± 0.16	11.20 ± 1.60	32.34 ± 0.91	2.53 ± 0.08	42.56 ± 1.81	0.40 ± 0.11	4.70 ± 0.36	+++	++	+	+	2.7
	CP1	0.47 ± 0.15	3.28 ± 0.18	12.82 ± 0.03	33.21 ± 0.26	2.31 ± 0.02	43.30 ± 0.35	0.53 ± 0.14	4.07 ± 0.22	+++	++	+	+	2.7
	CP2	0.70 ± 0.04	3.30 ± 0.10	12.49 ± 0.59	29.57 ± 0.03	2.32 ± 0.03	46.81 ± 0.43	0.42 ± 0.15	4.37 ± 0.12	+++	++	+	+	4.8
	CP3	0.50 ± 0.06	1.80 ± 0.17	9.15 ± 0.65	19.49 ± 0.74	1.18 ± 0.02	64.86 ± 0.30	0.43 ± 0.13	2.59 ± 0.24	+++	++	+	+	3.1
	NM4	0.21 ± 0.25	1.40 ± 0.04	3.62 ± 0.12	13.56 ± 1.33	0.69 ± 0.06	79.22 ± 1.20	0.24 ± 0.14	1.05 ± 0.11	+++	++	+	+	8.4

The number of pluses represents the abundance of mineral peaks. (C: calcite, Q: quartz, A: albite, M: muscovite)

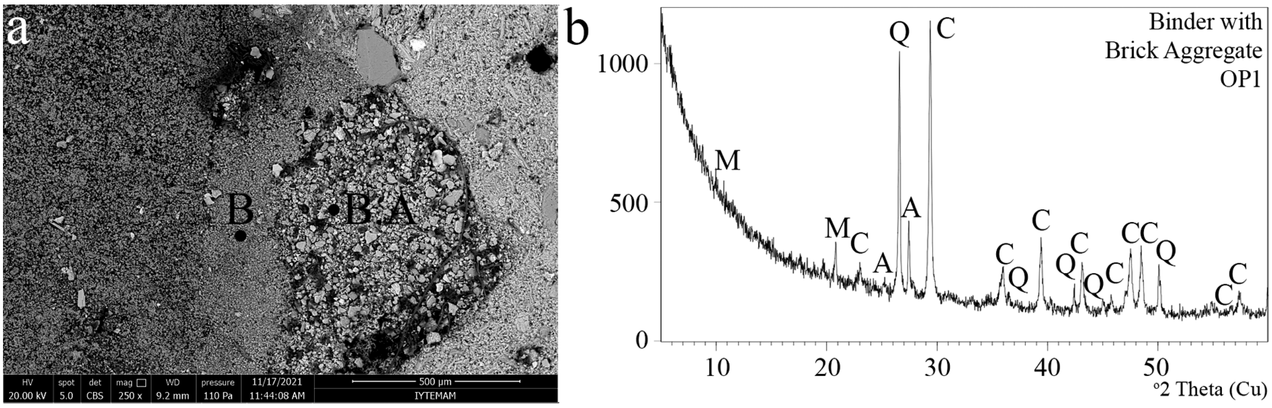

Figure 5: Binder (B) with a brick aggregate (B.A.) – sample OP1: a) SEM image 250×, b) XRD pattern (A: albite 76–1819, C: calcite 86–2334, M: muscovite 84–1302, Q: quartz 85–0798)

Table 4: Major oxide compositions of the binder and brick aggregate in sample OP1

	Major oxide compositions (*w*/%)							
	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Binder	0.61	4.32	5.89	17.65	0.88	68.35	0.10	2.20
Brick aggregate	1.13	4.15	17.35	38.94	3.36	29.58	0.48	5.02

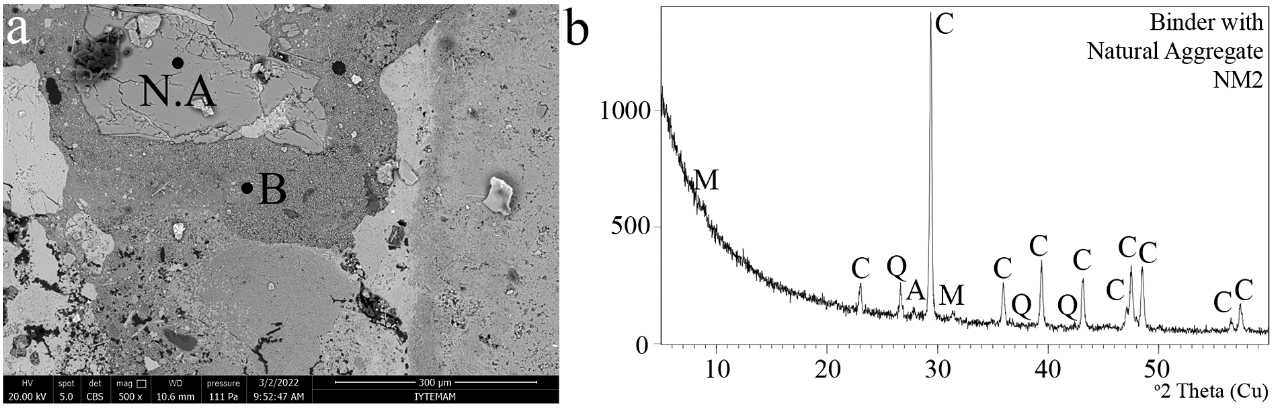

Figure 6: Binder (B) with a natural aggregate (N.A.) – sample NM2: a) SEM image 500×, b) XRD pattern (A: albite 76–1819, C: calcite 86–2334, M: muscovite 84–1302, Q: quartz 85–0798)

Table 5: Major oxide compositions of the binder and natural aggregate in sample NM2

	Major oxide compositions (*w*/%)							
	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Binder	0.56	1.07	2.84	21.94	1.46	71.50	0.13	0.50
Natural aggregate	0.11	0.22	0.46	95.09	0.27	3.86	0.00	0.00

ally bound water (H_2O) of the hydraulic products (CSH, CAH), while the losses between 600–900 °C were caused by a CO_2 release during the decomposition of carbonate lime. The CO_2/H_2O ratio between 1 and 10 indicated the hydraulic character of the mortars.[16] The CO_2/H_2O ratios were found to be between 5.2–10.0 by weight for the mortars composed of natural aggregates and between 2.7–4.8 by weight for the lime plasters composed of brick aggregates (**Table 3**). These results revealed that all the binders exhibited hydraulic properties. The hydraulicity of the binders may be attributed to the use of highly reactive natural and artificial pozzolanic aggregates in their production.

SEM images of the binders showed strong bonding between the lime and aggregates, which was an indicator of a pozzolanic reaction and hydraulic properties. Also, there was no microcrack formation or irregularity at the interfaces (**Figures 5a** and **6a**) (**Tables 4** and **5**).

4 CONCLUSIONS

Byzantine-period lime mortars and plasters used in different construction phases of the Anaia Church are stiff and compact materials that survived for centuries, preserving their original characteristics. All the lime mortars were produced from natural aggregates of a volcanic origin with lime/aggregate ratios between 1/2–5/3, whereas all the lime plasters consisted of brick aggregates with lime/aggregate ratios between 1/3–4/3. The only exception was the mortars used for the buttresses added to the church to strengthen its structure after the earthquakes in the 11th century, with a higher lime/aggregate ratio of 4/3–5/3.

Non-hydraulic and fat lime had been used for the mortar and plaster production after a long aging period. Natural aggregates of mortars were probably mainly obtained from the local rhyolite and dacite sources. Brick aggregates were manufactured from Ca-poor clays at low firing temperatures between 800–900 °C. All the natural and brick aggregates used in the mortars and plasters exhibited highly reactive pozzolanic properties. Due to the use of pozzolanic aggregates in their production, mortars and plasters had hydraulic characteristics.

It is remarkable that the basic physical properties, raw-material compositions, chemical and mineralogical compositions of the lime mortars and plasters used in different construction periods of the Anaia Church, which is a Byzantine structure, were similar and have not changed over the centuries. These similarities reveal that the knowledge of the use of the local raw-material resources and the mortar production technology was intentionally transferred over the centuries during the Byzantine period.

The production of new lime mortars and plasters to be used in the future conservation works in the Anaia Church should be physically, chemically and mineralogically compatible with the original mortar and plaster properties determined by this study. For this purpose, possible local lime, natural pozzolan and clay sources should be investigated and their suitability for the use in the mortar and plaster production should be fully examined. Furthermore, special production of brick aggregates should be carried out and these aggregates should be fired at low temperatures.

Acknowledgement

The authors would like to thank Prof. Dr. Zeynep Mercangöz and excavation team for their support in collecting samples from the ancient site of Kadıkalesi (Anaia). The authors also thank the Integrated Research Centers at the İzmir Institute of Technology for SEM-EDS, XRD and TGA analyses during the experimental phase of this investigation.

5 REFERENCES

[1] N. A. Davey, History of Building Materials, Phoenix House, London 1961

[2] J. A. H. Oates, Lime and Limestone: Chemistry and Technology, Production and Uses, Wiley-VCH, Weinheim 1998

[3] H. Böke, S. Akkurt, B. Ipekoğlu, E. Uğurlu, Characteristics of Brick Used as Aggregate in Historic Brick-Lime Mortars and Plasters, Cem. Concr. Res., 36 (**2006**), 1115–1122, doi:10.1016/j.cemconres.2006.03.011

[4] J. P. Adam, Roman Building Materials and Techniques, (1st pub. in 1937), Routledge, London and New York 2005

[5] Z. Mercangöz, Kuşadası, Kadıkalesi (Anaia), 1st ed., Ege Üniversitesi Yayınları, İzmir 2012

[6] M. B. Kanmaz, B. İpekoğlu, Restorations due to Earthquakes in the Ancient Cities: Anaia Byzantine Church, Kargir Yapılarda Koruma ve Onarım Semineri VIII, 2016, 189–205

[7] C. Foss, Ephesus after Antiquity: A Late Antique, Byzantine and Turkish City, Cambridge University Press, New York 1979

[8] P. Culerrier, Les évêchés suffragants d'Éphèse aux 5e-13e siècles, Rev. Etud. Byz., 45 (**1987**) 1, 139–164, doi:10.3406/rebyz.1987.2207

[9] Z. Mercangöz, The Variable Historical Destiny of Anaia as Emporion and Kommerkion, I. Uluslararası Sevgi Gönül Bizans Araştırmaları Sempozyumu, 2010, 279–292

[10] H. Soysal, S. Sipahioğlu, D. Kolçak, Y. Altınok, Historical Earthquake Catalog of Turkey and its Surroundings (BC 2100–AC 1900), Tübitak Yayınları, İstanbul 1981

[11] M. B. Kanmaz, Evalation of Conservation Problems of Anaia Byzantine Church, Kadıkalesi, Kuşadası, Izmir Institute of Technology, 2015

[12] RILEM:1980 – Tests Defining the Structure, Vol. 13, No. 73

[13] E. C. Eckel, Cements, Limes, and Plasters: Their Materials, Manufacture, and Properties, 1st ed., John Wiley & Sons, New York 1905

[14] R. S. Boynton, Chemistry and Technology of Lime and Limestone, John Wiley & Sons, 1966

[15] M. P. Luxan, F. Madruga, J. Saavedra, Rapid Evaluation of Pozzolanic Activity of Natural Products by Conductivity Measurement, Cem. Concr. Res., 19 (**1989**) 1, 63–68, doi:10.1016/0008-8846(89)90066-5

[16] A. Bakolas, G. Biscontin, A. Moropoulou, E. Zendri, Characterization of Structural Byzantine Mortars by Thermogravimetric Analysis, Thermochim. Acta, 321 (**1998**), 151–160, doi:10.1016/s0040-6031(98)00454-7

[17] E. Uğurlu, H. Böke, The Use of Brick–Lime Plasters and Their Relevance to Climatic Conditions of Historic Bath Buildings, Constr. Build. Mater., 23 (**2009**) 6, 2442–2450, doi:10.1016/j.conbuildmat.2008.10.005

[18] Ö. Aslan Özkaya, H. Böke, Properties of Roman Bricks and Mortars Used in Serapis Temple in the City of Pergamon, Mater. Charact, 60 (**2009**) 9, 995–1000, doi:10.1016/j.matchar.2009.04.003

[19] ASTM C618-03, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete (**2003**)

[20] J. Lanas, J. I. Alvarez, Masonry Repair Lime-Based Mortars: Factors Affecting the Mechanical Behavior, Cem. Concr. Res, 33 (**2003**) 11, 1867–1876, doi:10.1016/S0008-8846(03)00210-2

[21] A. El-Turki, R. J. Ball, M. A. Carter, M. A. Wilson, C. Ince, G. C. Allen, Effect of Dewatering on the Strength of Lime and Cement Mortars, J. Am. Ceram. Soc., 93 (**2010**) 7, 2074–2081, doi:10.1111/j.1551-2916.2010.03667.x

[22] E. Aggelakopoulou, A. Bakolas, A. Moropoulou, Properties of Lime-Metakolin Mortars for the Restoration of Historic Masonries, Appl. Clay Sci., 53 (**2011**)1, 15–19, doi:10.1016/j.clay.2011.04.005

[23] A. Gameiro, A. Santos Silva, P. Faria, J. Grilo, T. Branco, R. Veiga, A. Velosa, Physical and Chemical Assessment of Lime-Metakaolin Mortars: Influence of Binder:Aggregate Ratio, Cem. Concr. Compos, 45 (**2014**), 264–271, doi:10.1016/j.cemconcomp.2013.06.010

[24] A. M. S. Loureiro, S. P. A. da Paz, M. R. do Veiga, R. S. Angélica, Investigation of Historical Mortars from Belém Do Pará, Northern Brazil, Constr. Build. Mater., 233 (**2020**), doi:10.1016/j.conbuildmat. 2019.117284

[25] A. Bakolas, G. Biscontin, A. Moropoulou, E. Zendri, Characterization of the Lumps in the Mortars of Historic Masonry, Thermochim. Acta, 269 (**1995**), 809–816, doi:10.1016/0040-6031(95)02573-1

[26] S. Bruni, F. Cariati, P. Fermo, P Cairati, G. Alessandrini, L. Toniolo, White Lumps in Fifth- to Seventeenth-Century AD Mortars from Northern Italy, Archaeometry, 39 (**1997**) 1, 1–7, doi:10.1111/j.1475-4754.1997.tb00786.x

[27] L. Barba, J. Blancas, L. R. Manzanilla, A. Ortiz, D. Barca, G. M. Crisci, D. Miriello, A. Pecci, Provenance of the Limestone Used in Teotihuacan (Mexico): A Methodological Approach, Archaeometry, 51 (**2009**) 4, 525–545, doi:10.1111/j.1475-4754.2008.00430.x

[28] I. C. Zamba, M. G. Stamatakis, F. A. Cooper, P. G. Themelis, C. G. Zambas, Characterization of Mortars Used for the Construction of Saithidai Heroon Podium (1st Century AD) in Ancient Messene, Peloponnesus, Greece, Mater. Charact, 58 (**2007**), 1229–1239, doi:10.1016/j.matchar.2007.07.004

[29] R. W. Le Maitre, A. Streckeisen, B. Zanettin, M. J. Le Bas, B. Bonin, P. Bateman, G. Bellieni, A. Dudek, S. Efremova, J. Keller, J. Lameyre, P. A Sabine, R. Schmid, H. Sørensen, A. R. Woolley, Igneous Rocks. A Classification and Glossary of Terms, 2nd ed., Cambridge University Press, New York 2002

[30] D. Miriello, A. Bloise, G. M. Crisci, C. Apollaro, A. La Marca, Characterisation of Archaeological Mortars and Plasters from Kyme (Turkey), J. Archaeol. Sci., 38 (**2011**) 4, 794–804, doi:10.1016/j.jas. 2010.11.002

[31] C. Helvaci, Geological Features of Neogene Basins Hosting Borate Deposits: An Overview of Deposits and Future Forecast, Turkey, Bull. Miner. Res. Explor., 151 (**2015**), 169–215, doi:10.19111/bmre. 05207

[32] E. Uğurlu Sağın, H. E. Duran, H. Böke, Lime Mortar Technology in Ancient Eastern Roman Provinces, J. Archaeol. Sci. Reports, 39 (**2021**), 1–14, doi:10.1016/j.jasrep.2021.103132

[33] P. Cardiano, S. Ioppolo, C. De Stefano, A. Pettignano, S. Sergi, P. Piraino, Study and Characterization of the Ancient Bricks of Monastery of "San Filippo Di Fragalà" in Frazzanò (Sicily), Anal. Chim. Acta, 519 (**2004**), 103–111, doi:10.1016/j.aca.2004.05.042

[34] S. Lee, Y. J. Kim, H. S. Moon, Phase Transformation Sequence from Kaolinite to Mullite Investigated by an Energy-Filtering Transmission Electron Microscope, Journal of the American Ceramic Society, 82 (**1999**) 10, 2841–2848, doi:10.1111/j.1151-2916.1999.tb02165.x

[35] B. Middendorf, J. J. Hughes, K. Callebaut, G. Baronio, I. Papayianni, Investigative Methods for the Characterisation of Historic Mortars – Part 2, Chemical Characterisation, Mater. Struct., 38 (**2005**) 282, 771–780, doi:10.1617/14282