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AN EVALUATION OF BINDERS AND AGGREGATES USED IN ARTIFICIAL STONE ARCHITECTURAL CLADDINGS AND ELEMENTS IN LATE 19TH - EARLY 20TH CENTURIES

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1. This article is prepared resting on the research titled "Geç Osmanlı - Erken Cumhuriyet Dönemi Mimarlığında Kullanılan Yapay Taşların Bağlayıcı ve Agrega Oran ve Türlerinin Analizi ve Koruma Bilimi Açısından Değerlendirilmesi", undertaken by Prof. Dr. Ahmet Ersen at İTÜ (İTÜ BAP A_32.142).

The material defined as 'artificial stone', frequently used on the façades of the late 19th and early 20th century buildings, is a mixture of binder, aggregate and other additives and may either be applied directly as a coating on wall surfaces or precast in moulds and then attached to façades as decorative architectural elements (**1**). One of the effects of the Industrial Revolution in the 19th century was a tendency to standardize architectural production, which in turn moved away from time-consuming and costly traditional techniques in search of those in accordance with the dynamic social, economic and cultural structure of the period. One of the resulting solutions was the rapidly mass-produced artificial stones that replaced the traditional stone masonry.

The aim of this research is to evaluate the use of artificial stone on the exterior façades of buildings dated to turn of the last century in terms of architecture and conservation science, focusing on the classification of their constituent binders and aggregates. The experiments, conducted according to related national and international standards based on research programs recommended for similar mortar and plaster samples in literature, enabled the determination of the physical, raw material and mineralogical characteristics of the samples. Results indicate that all the binders have hydraulic quality, some being artificial cements and/or natural water limes and others being fat limes, mixed with mostly artificial pozzolanic additives. The identification of calcium sulphate enabled the classification cements as opposed to limes. Compared to mortars and concretes, the aggregates are smaller in size and usually lighter in colour, such as white sand, and crushed marble and lime stone. The use of fibrous aggregates as well as artificial pozzolanic aggregates with hydraulic binders including cements, on the other hand, may indicate the continuity of tradition and/or distrust in these new materials.

INTRODUCTION

'Artificial stones' frequently encountered on the exterior façades of historicist and eclecticist architecture in late 19th and early 20th centuries, are stone-imitating plasters composed of binders, aggregates and other additives, which may either be applied as a coating on wall surfaces or precast in moulds and then attached to façades as decorative architectural elements.

Introduction and development of this innovative material and technique in architecture could not have been possible without the development and wide-spread production of hydraulic binders and various mixtures prepared thereof. Although practically known since the Romans, the hydraulic setting mechanisms were scientifically understood only in the second half of the 18th century and natural cements were differentiated from lime stones depending on their chemical content. As a result, artificial production methods for various types of hydraulic limes and cements were developed and patented in early 19th century, and began to be produced in industrial scale by mid 19th century. Thus, by the second half of the same century, various types of artificial hydraulic limes and cements were commonly used in all types of construction activity, both supplementing traditional materials and techniques and resulting in the development of new ones. While high-strength and high-durability hydraulic binders were used in great engineering works, various types of lower-cost cements were employed extensively in the production of architectural and decorative elements, replacing stone according to the aesthetical understanding of the period: "Our fathers had a Paris of stone; our sons will have one of plaster" (Victor Hugo, 1832).

This transformation in European architectural practice was soon reflected on its periphery, including the Ottoman Empire. The technological modernization of the empire that began at the end of the 17th century, also affected the field of building and construction, and the 19th century saw a transformation in theory and practice as architecture was recognized as a separate field, construction activity was institutionalized, its control was regularized and its education was systematized. As a result of new building and fire regulations and the rapidly increasing population, multiple-storey brick masonry structures became more common in İstanbul, completely replacing traditional timber-frame houses especially in developing and dense urban areas. The design and erection of comparatively more complex masonry structures as well as their *Beaux-Arts* façades required the practical intervention of schooled architects and institutionalized constructors. Active architects educated abroad brought this new aesthetics as well as new materials and technologies, including cements, concrete, precast elements and artificial stone applications to the Ottoman capital.

Although written sources and diverse archive documents dating from the period in İstanbul are very limited compared to the vast amount available for Europe and North America, the existing buildings in various parts of the city themselves form the main body of invaluable and original evidence. It is possible to analyse these late 19th - early 20th century buildings in order to evaluate the architectural characteristics of their exterior façades and decorative programs, the distribution and use of artificial stones, the design of architectural elements according to various orders and styles and the materials and techniques utilized.

EXPERIMENTAL WORK

Buildings chosen for sampling and analyses were formerly unrepaired or restored masonry structures, located in those urban areas of İstanbul, which had been developed and/or extensively renewed, e.g., as a result of fire, during the second half of the 19th and the first quarter of the 20th centuries, including mostly but not only Galata-Beyoğlu and Fener-Balat. The selection was also based on the availability of archive material for dating such as historic maps as well as architectural quality in terms of reflecting the aesthetic understanding of the period and originality of design, characteristics, variety and richness of the decorative program (**Table 1**). The artificial stone techniques encountered include stone imitating plasters, decorated with knife-cut joints and stamp-moulds, plaster cornices and friezes produced in-situ with running moulds and precast elements with deeper profiles or reliefs, probably produced in the workshop.

The samples were analysed and evaluated according to the experimental work programs proposed in related publications to determine their physical, material and mineralogical characteristics based on national and international standards.

Visual Characteristics

The substrates underneath the plasters were brick masonry walls in all examples. The binders were generally in shades of grey, but also included white, pink/white, light yellow and beige matrices, the top or finishing layers or single-layer plasters generally having a lighter colour. Grey and beige shades indicate that the binders are probably cementitious, whites may be water or air limes and pink shows the presence of brick dust. The thicknesses of layers showed great variety and could not be determined exactly in some cases (**Table 2**). Bottom or rough layers were usually thicker (max. 5cm) than top or finishing layers (min. 2mm). The radii of the aggregates were directly related to the thickness and location of the layers: The rough layers generally included larger aggregate sizes compared to finishes. Crushed brick as well as brick dust and various types of ashes including charcoal, slag, cinder, etc. were common ingredients. Also various organic fibres, including straw and perhaps hair were frequently used. The surfaces were meant to be exposed and left unpainted in most cases.

Physical Characteristics

The densities ranging between 1.70-2.60 g/cm^3 are normal for mortars and/or plasters with hydraulic binders. The similarity of the aggregates to those used with non-hydraulic binders indicates that the higher densities are due to the use of cements and/or water limes as binders and/or that the binder/aggregate ratios are different. The porosities are also lower than those of lime mortars (Franzini et al., 2000; Moropoulou et al., 2003; Böke et al., 2006; Tunçoku ve Caner-Saltık, 2006; Güleç, 1992; Baturayoğlu Yöney, 2008). The pores are usually circular and/or polygonal in shape and were flattened into ellipsoidal forms in those examples where the plasters were compressed.

Raw Material Composition

The raw material compositions were determined with the "acid loss" method (Jedrzejevska, 1981; Teutonico, 1988; Middendorf et al., 2005). The lime contents of the plaster mixtures range between 20-40% (Table

Sample No	Building Name /Address	Date	Sample Description			
			Location / Floor level	Architectural definition	Technique	Number of layers
01.GR	Kamondo Apartmanı/Hanı, Serdar-ı Ekrem Sokak 30-40 (Apparts. Camondo)	1861-1868, 1870-1876	G	stone-imitating plaster	knife-cut joints	1
02.YC	Beyoğlu İstiklal Caddesi Haco Pulo Pasajı (Apparts./Passage Hazzopoulo 12)	1871, 1890, 1905	1	plaster window jamb	running mould	1
03.IC	Türkiye İş Bankası Müzesi, eski Yenicami Şubesi (Bureaux de la Poste Ottomane)	1892	G	plaster panel below window	stamp mould	1
04.YR	Beyoğlu Büyük Ada Han, (Block 307, Lot 1; Asmalımescit, on the corner of Meşrutiyet and General Yazgan streets; Apparts. Camondo)	before 1905	3	plaster	undecorated	2
05.BR	Balat Vodinya Street 39	late 19th cent.	1 below projection	stone-imitating plaster	knife-cut joints	1
06.BR	Balat Akçın Street 17 – Yaldızlı Street 18	late 19th cent.	1	plaster frieze	running mould	1
07.BR	Balat Kırıktulumba Street 4	late 19th cent.	G	plaster door jamb	running mould	2
08.BR	Balat Ayan Street 14-18-22	late 19th cent.	2	plaster door jamb	running mould	1
09.BR			2	plaster window jamb	running mould	1
10.BR			2	plaster panel below window	precast/ stamp mould	1
11.SP	Üsküdar Atpazarı Police Station, public bldg.	late 19th cent.	1	plaster frieze	running mould	1
12.YR	Beyoğlu Halas Sokak 31	before 1905	G	fluted pilaster, plaster	running mould	2
13.GR	Galata Serdar-ı Ekrem Street 42 (*Apparts. A. Kastro, Şükrü Bey Han/Apartmanı*)	before 1905	G	stone-imitating plaster	knife-cut joints	2
14.GR	Galata Müellif Street 10 (*Apparts. Nersessian /Nersesyan Apartmanı*)	before 1905	G	stone-imitating plaster	knife-cut joints	1
15.YR	Beyoğlu Yeşilçam Sokak 27 (*Apparts. Castorides*)	before 1905	G	stone-imitating plaster	knife-cut joints	1
16.YR	Beyoğlu Garanti Platform (İstiklal Street 276, *Apparts. Siniossoglou*)	before 1905	G	plaster frieze	running mould	3
17.YR			G	plaster frieze	running mould	2
18.AR	Arnavutköy Memduh Paşa Armoury and Library Pavillion, (architect: Raimondo D'Aronco)	1904	G-1	stone-imitation panel	precast	3
19.BR	Balat Hızırçavuş Köprüsü Street 2	early 20th cent.	G	stone-imitating plaster	knife-cut joints	1
20.BR			B	stone-imitating plaster	knife-cut joints	2
21.BR	Balat Vodinya Street 96	early 20th cent.	G	stone-imitation panel	precast	3
22.BR	Balat Yıldırım Street 32	early 20th cent.	1	artificial marble, plaster	knife-cut joints	2
23.GC	T. İş Bank Galata Branch, Bankalar Street 27-29	1918	1	pilaster base	precast	1

Sample coding: B: Balat, G: Galata, Y: Beyoğlu, S: Üsküdar, İ: İstanbul, A: Arnavutköy;
R: residential, C: commercial, P: public
Location: B: basement, *sous bassement*; G: ground floor; 1: first floor; 2: second floor, etc.

Table 1. Sampled buildings, general information and observations.

Sample No	Thick-ness	Acid loss lime content (%)	Ignition loss			Binder	Aggregates	Additives	Binder type	B/A ratio (m)
			SW loss (%)[1]	CO_2 loss (%)[2]	CO_2/SW loss ratio					
01.GR	--	40.86	3.23	4.78	1.48	Ct, G, Mt	Q, F, S, O	B, A, Fb	C	%20-25
02.YC	--	48.89	8.03	15.67	1.95	Ct, G	Q, F	B, A, Fb	L	%30-35
03.IC	~2.00cm	33.44	3.46	15.64	4.52	Ct	Q, F, S	B(±), A, Fb	HL	%25-30
04.YR.b	1.25cm	33.10	2.52	11.64	4.62		Q, Ct, M	B, A	HL/C	%25-30
04.YR.t	0.30cm	32.68	3.62	6.85	1.89		Q, Ct	A	C/PC	%20-25
05.BR	0.45cm	78.43	--	--	--	--	Q, Ct/M, F, S	B, A, Fb	HL	%35-40
06.BR	--	41.02	6.77	6.17	0.91	Ct, G	Q, F, S	B, A, Fb	L	%25-30
07.BR.b	~1.00cm	29.64	--	--	--	--	Q, Ct, F, S	B(±), A	HL	%20-25
07.BR.t	0.35cm	41.28	--	--	--	--	Q, Ct, F, S	B(±), A	HL	%35-40
08.BR	--	39.79	--	--	--	Ct	Q, F	B, A	C	%20-25
09.BR	--	40.09	--	--	--	--	Q, Ct, V	B, A	C	%30-35
10.BR	--	27.48	--	--	--	--	Q, Ct, V	B, A, L	C	%35-40
11.SP	--	48.26	7.49	14.17	1.89	--	Q, F	B, A, Fb,	L	%30-35
12.YR.b	--	27.74	4.09	8.03	1.96	Ct	Q, F	B, A(±), Fb,	L	%30-35
12.YR.t	--	33.46	2.89	13.20	4.57	Ct, G	Q, F, S	B, A	HL/C	%20-25
13.GR.b	0.90cm	28.69	1.96	18.75	9.57		Q, V	A, Fb	L	%30-35
13.GR.t	2.06cm	29.10	2.31	6.69	2.90		Q, Ct	B, Fb	HL	%20-25
14.GR	~2.00cm	15.63	1.93	10.38	5.38		Q, Ct, S	B(±), A	HL	%20-25
15.YR	--	28.56	3.72	5.18	1.39	Ct, G, Mt	Q, F, S	B, A(±), Fb	C	%20-25
16.YR.b	--	48.50	14.56	30.67	2.11	--	Q, F, V	B, Fb	HL/C	%30-35
16.YR.m	--	46.49	9.04	25.66	2.84	--	Q, F	B, Fb	HL/C	%30-35
16.YR.t	0.40cm	--	--	--	--	--	C, M	A	HL	%35-40
17.YR.b	--	44.50	--	--	--	--	Q, V, S	--	HL/C	%30-35
17.YR.t	0.20cm	--	--	--	--	--	M, Ct	--	HL	%25-30
18.AR.b	3.75cm	20.24	2.68	5.37	2.00	Ct	Q, F, S	B, A, Fb	C	%20-25
18.AR.m	0.60cm	37.82	2.77	7.70	2.78	Ct, Mt	Q, F, S	B, A, Fb	HL	%30-35
18.AR.t	0.20cm	36.89	5.09	10.85	2.13	Ct, G	Q, F	B, A	C	%30-35
19.BR	--	21.57	2.64	4.61	1.75	--	Q, V, Ct	B, A	HL	%20-25
20.BR.b	--	25.05	5.36	8.30	1.55	Ct, G	Q, F	B, A, Fb	C	%25-30
20.BR.t	~0.60cm	33.25	7.38	9.41	1.27	Ct, G, Mt	Q, F, S, O	B, A, Fb	C	%35-40
21.BR.b	0.30cm	31.06	--	--	--	Ct	Q, F	B, A	C	%20-25
21.BR.m	1.00cm	30.83	--	--	--	Ct	Q, F, S	B, A(±)	C	%20-25
21.BR.t	0.30cm	44.15	--	--	--	Ct, G	Q, F	B, A	C	%35-40
22.BR.b	~1.00cm	49.16	4.86	8.96	1.84	Ct, G	Pt, Q, F	B, A, Fb	C/PC	%35-40
22.BR.t	~1.70cm	73.17	3.77	25.88	6.86	Ct, CS	Pt, M	B, A, Fb	C/PC	%35-40
23.GC	--	55.70	--	--	--	Ct, G	Q, F, Ct/M	B, A(±),Fb	HL/C	%35-40

Sample coding: B: Balat, G: Galata, Y: Beyoğlu, S: Üsküdar, İ: İstanbul, A: Arnavutköy;
R: residential, C: commercial, P: public
Layer coding: b: bottom, rough, m: middle, t: top, finishing; coded only if there are more than one layers.
Ignition loss: 1: structural water loss occurs between 105-550°C; 2: CO_2 loss between 550-1050°C
Binder: Ct: calcite ($CaCO_3$), G: gypsum ($CaSO_4.2H_2O$), Mt: magnetite ($MgCO_3$), CS: calcium silicate $Ca_2(SiO_4)$
Aggregates: Q: quartz (SiO_2), V: volcanic, F – feldspars ($Na(AlSi_3O_8$ $KAlSi_3O_8)$), Ct: carbonates, lime stone,
M: marble, S: shells and fossils, Pt: Portlandite ($Ca(OH)_2$), O: opal (SiO_2. nH_2O)
Additives: A: ash, charcoal, cinder, etc., B: brick particles and dust, O: opal (natural pozzolan), Fb: organic fibres
Binder types: L: air (fat) limes, HL: water limes or hydraulic limes, C: cements, PC: Portland cement

Table 2. Analysis results and evaluation.

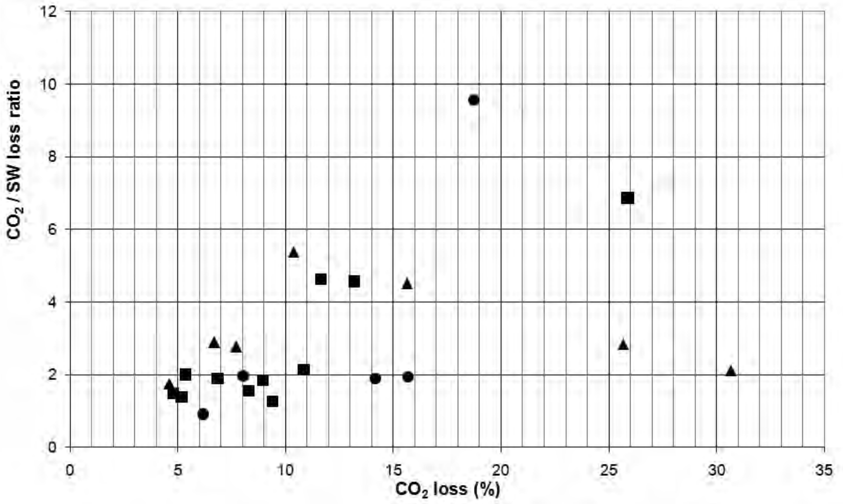

Figure 1. Ignition loss results: CO_2 loss against CO_2/SW loss (■ cements, ▲ water limes, ● fat limes).

2) and are much lower compared to traditional lime mortars with ratios ≥50% (Böke et al., 2006; Franzini et al., 2000; Moropoulou et al., 2003; Tunçoku ve Caner-Saltık, 2006; Tunçoku, 2001; Güleç ve Ersen, 1998; Güleç, 1992), which indicate their hydraulicity. The relatively higher lime content in some samples (35-50%) is consistent with the matrices observed in petrography (characteristic lighter colours and the presence brick dust and ashes): This is either an indication of the use of a fat lime mortar with pozzolanic additives (e.g. 02.YC, 06.BR, 11.SP) or water lime (e.g. 07.BR.t, 16.YR.b, 16.YR.m, 17.YR.b). However, in those cases where the binders are cementitious, similar results may also arise from the presence of calcareous aggregates in the matrix, such as calcites, shells and marble (e.g. 01.GR, 08.BR, 09.BR, 18.AR.m, 18.AR.t, 21.BR.t, 22.BR.b). Finishing layers with grey or beige matrices appear to have larger ratios of light coloured aggregates to imitate stone. The use of marble or lime stone ballast as the only type of aggregate as in imitation marbles, may raise the lime content as high as the 50-80% range (e.g. 05.BR, 22.BR.t, 23.GC).

The aggregates insoluble in acid were visually analysed after sieving to determine their types and sizes. Those samples with similar acid loss percentiles also have similar aggregate size distribution curves. Compared to Fuller curves defined as ideal for concrete mixtures, the large and small radii aggregate ratios are lower while medium radii aggregate ratios are higher in plasters. However, the similarity of the curves for top and bottom layers shows that the ideal distributions are essentially the same for rough plasters and finishes. The radii are below 8mm in rough and 4mm in finishing layers, which are defined as small-radius aggregates in TS 706 EN 12620 (2003).

The aggregates and other additives consist of quartz and quartzite, various opaque minerals including calcites, feldspars and volcanic rocks, brick ballast and dust, ashes and organic fibres. Natural aggregates are generally angular in form. Pragmatic historic and early modern sources (e.g. Millar, 2004: 462-3) state that angular quarry sand and ballast bond better with binders compared to rounded river and sea sands. The presence of terra cotta (brick, tile, pottery, etc.) ballast and dust and/or ashes (coal, charcoal, various organic ashes, cinder and inorganic slag) is observed in all samples except 17.YR. These materials have been used as artificial pozzolans since the Roman period (Vitruvius, 1990: 145-7; Raymond, 1908: 100-105; Vicat, 1997: 89-90; Pasley, 1997: 2-4, 162). Ashes also lower the densities of plasters and/or precast elements and provide fire resistancy (*Blocs et Murs en Béton,* 1930; Millar, 2004: 369, 480-97). The use of brick dust and ash together in almost all samples (except for 04.YR.t, 13.GR.b, 16.YR.t which do not contain brick dust and 13.GR.t, 16.YR.b, 16.YR.m which do not contain ash) indicate that traditional lime mortar additives were still indispensible in this period of transition although the new binders were hydraulic. The presence of organic fibres, which have been utilized to increase the durability of plasters against shrinking stresses since ancient times (Sickles, 1981) with hydraulic binder is also interesting, and may be considered as a traditional continuity into the early modern period (e.g. Millar, 2004: 79-80; Verall, 2000, I: 63-4); synthetic fibres are used for the same purpose today. The colour and characteristics of the dust sized particles left on the filter paper after wet sieving of the acid solution also provide information concerning binders: Pink indicates the presence of brick dust whereas shades of white and grey show that there are dehydrated parts left from hydraulic binders insoluble in acid.

Ignition loss analyses were conducted in order to provide information on the hydraulicity of the binder parts. Dehydration losses occur from calcium silicate and aluminate hydrates between 105-550°C and carbon dioxide loss occurs from calcites due to carbonation between 550-1050°C. The CO_2/SW loss ratios below 10 indicate hydraulicity in binder samples (Biscontin et al., 2002; Moropoulou et al., 2003; Moropoulou et al., 2005; Genestar et al., 2006; Pecchioni et al., 2005). The calculated ratios between 1-3 (Table 2; Fig. 1) indicate that the binders tested are indeed hydraulic. The relatively higher ratios observed in 03.IC, 12.YR.t and 14.GR must be due to the presence of a larger amount of calcareous aggregates including shells and in 04.YR.b and 22.BR.t due to that of marble ballast. In 13.GR.b, however, the high ratio probably arises from the presence of free lime.

The structural water (SW) loss in lime mortars between 100-550°C is less than 4% whereas it is 4-8% in traditional fat lime mortars with artificial pozzolans (brick ballast and dust) and above 8% in hydraulic lime mortars with natural or artificial pozzolans. However, as these values may change in relation with lime/aggregate ratios, for a more reliable evaluation CO_2/SW loss ratios and CO_2 loss are compared (Table 2; Fig. 1; Moropoulou et al., 2003). Whether cementitious or not, the binders have hydraulicity according to the results. The irregularities are probably due to higher free lime contents, either in the binder parts or in calcareous aggregates.

The mineralogical structures of the binders were determined with X-ray diffraction (XRD). The XRD patterns show calcium carbonate peaks due the carbonation of the lime content (see Fig. 2a). Some samples also included magnesium hydroxide as well as dolomite, magnesium carbonate and gypsum formed as a result of the reaction of calcium magnesium hydroxide and anhydrite gypsum with water and the carbon dioxide in air. There were also trace minerals arising from aggregates such as quartz, albite, feldspar etc. The results are similar to those in other sources (e.g. Pecchioni et al., 2005).

Water limes have been prepared by firing lime stones with 10-25% clay content over 900°C in kilns since the end of 18th century. The resulting product is quick lime (CaO) and di-calcium silicate ($2CaO.SiO_2$, C_2S). The high content of lime leaves higher ratios of free lime in the binder and thus they set both with the effect of water and air. Stronger hydraulic binders classified as Roman cements do not have free lime content and set only with the effect of water; these are formed of di-calcium silicate (2CaO. SiO_2, C_2S) as the firing occurs between 900-1200°C (Sabbioni et al., 2001; Masazza, 2004). Portland cements, on the other hand, are fired at 1200-1450°C and include high ratios (60%) of tri-calcium silicate (3CaO.SiO_2, C_3S) (*Decorated Renders*, 1999: 119**)**. The basic minerals in cement are C_3S, C_2S, tri-calcium aluminate (C_3A) and aluminoferrite (C_4AF). Anhydrite cement is composed of *c.* 75% C_2S and C_3S. When cement reacts with water, colloidal calcium-silicate-hydrate (C-S-H) and calcium hydroxide (CH, portlandite) are formed. C_3S reacts more quickly than C_2S, releasing large amounts CH and playing an important role in the development of early mechanical strength. Amorphous gelatinous C-S-H structures cannot be observed in XRD analyses. The binder of a matured Portland cement mortar or concrete includes 60-70% C-S-H, 25% CH, 10% monosulphate hydrates (AFm) and trace amounts of hydro-garnates (Pecchioni et al., 2005; *Decorated Renders*, 1999, 120). Similarly C_2S in hydraulic lime also transforms into colloidal C-S-H and CH due to hydration. CH transforms into calcium carbonate reacting with the carbon dioxide in air and may be observed in XRD patterns as its structure is not amorphous. The higher calcite peaks observed in some of the XRD patterns may arise from the addition of free lime to hydraulic mixtures.

It was possible to identify the cements using the XRD results, based on the presence of gypsum (**Table 2**). It is known that *c*. 5% gypsum is added to the cement clinker before grinding during production in order to control the setting of the cement mortars (Eckel, 2005, 200-67) since Johnson's Portland cement in the 1850s. On the other hand, gypsum is not a necessary ingredient for hydraulic limes as it yields C_2S when setting.

Magnesite ($MgCO_3$; **Table 2**) observed in some of the samples, is known to increase the mechanical strength of lime mortars (Vicat, 1997, 175-6; Burn, 2001: 50; Cowper, 1998, 52). There were calcium silicate peaks in one sample (22.BR.t; Figure 2a) which show that the mortar has not been fully hydrated. The two layers of sample 22.BR, both of which have high ratios of calcite also had CH, indicating that the diffusion of carbon dioxide into the plaster was prevented by the carbonation of the upper section. Opal, observed in two samples (01.GR and 20.BR.t) is a natural pozzolan (Tunçoku and Caner-Saltık, 2006).

Petrography

The petrographical characteristics of the binders, aggregates, their visual characteristics and aggregate-binder interfaces were studied and approximate binder/aggregate ratios were determined by observing the thick and thin sections under binocular and polarizing microscopes. The binder-aggregate bonding is strong in all samples and there are no empty spaces between aggregate particles (**Figure 2b, 2c**), showing that the plasters were well-mixed. The mixtures are generally composed of 1 part binder and 3 parts of aggregates (**Table 2**). The angularity and surface roughness of the aggregates enable better binder adhesion and provide higher mechanical strength.

The binders are mostly composed of amorphous gelatinous silicates, indicating that they are hydraulic, whether cements, water limes or lime and cement mixtures (**Table 2**). The gelatinous silicates are usually grey in colour in the cementitious samples (01.GR, 04.YR.b, 04.YR.t, 08.BR, 09.BR, 10.BR, 15.YR, 17.YR.b, 18.AR.b, 18.AR.t, 20.BR.b, 20.BR.t, 21.BR.b, 21.BR.m, 21.BR.t, 22.BR.b, 22.BR.t). The water limes are lighter in colour (03.IC,

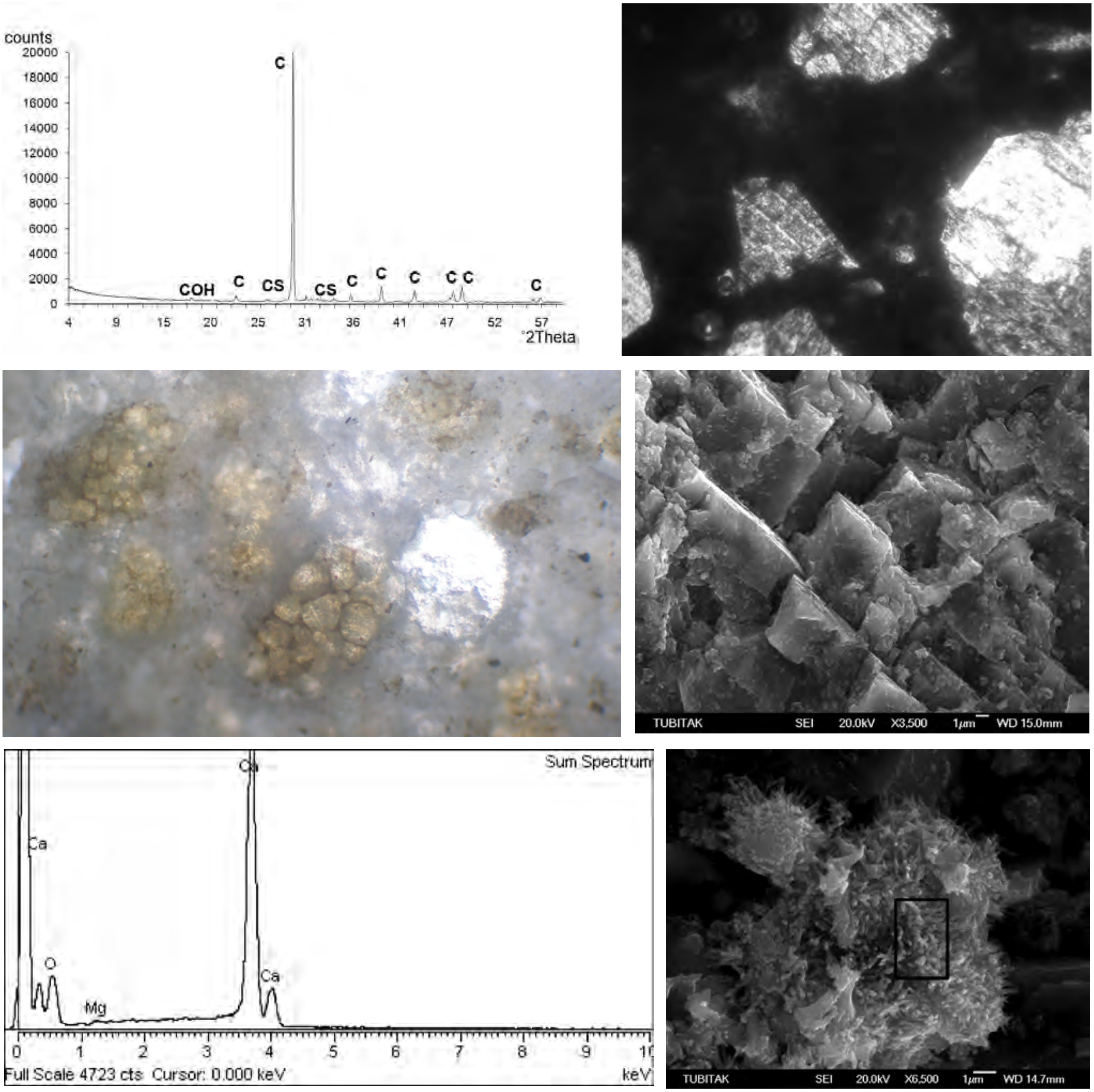

Figure 2. Sample 22.BR.t (from top to bottom): (a) XRD pattern showing prominent calcite (C) peak as well as calcium sulphate (CS) and calcium hydroxide (CH) peaks; thin section images under polarizing microscope: (b) general matrix showing angular marble ballast (DN, 4x) and (c) belite (C_2S) crystals (DN, 60x).

Sample 22.BR.t, binder part: (d) SEM image (3,500x, SEI) showing calcite crystals and (e) its EDS spectrum; (f) SEM image (6,500x, SEI) showing C-S-H crystals and (g) its EDS spectrum.

12.YR.t, 13.GR.t, 14.GR, 16.YR.b, 16.YR.m, 18.AR.m, 19.BR, 23.GC) whereas limes with artificial pozzolanic additives are pinkish (02.YC, 06.BR, 11.SP, 12.YR.b, 13.GR.b). The binder types were determined depending on XRD and petrography results (Table 2). The binder/aggregate ratios, determined by vectoral analysis of microscopic images (Table 2; approx. mass %; RILEM TC167 COM 1, 2001), range between 20-40%, with 20-30% in rough and 30-40% in finishing layers. The binder ratios are generally higher in finishing layers and where the binders are fat limes (e.g. 12.YR.b). Due to the presence of calcareous aggregates in almost all samples, the lime ($Ca(OH)_2$) loss ratios obtained in acid loss analysis are higher compared to the binder ratios observed in petrography. The difference is more pronounced in two samples (22.BR.t and 23.GC) which contain marble ballast and no quartz or quartzite.

Chemical and Structural Characteristics

The chemical composition of the aggregates and the structural characteristics of the binder matrices were determined by SEM-EDS analysis. The binders are composed of high ratios of calcium, silica and low amounts of aluminium, indicating that they are formed of calcium silicates and are indeed hydraulic. Aggregates, on the other hand, are mostly composed of silica and alumina (as observed in XRD and petrography) and trace amounts of calcium must result from the calcite in the binders and calcareous aggregates.

Binder-aggregate adhesion is high as observed in petrography (**Figure 2b, 2c**), increasing physical durability and mechanical strength. The precipitated calcite crystals in the binder parts (**Figure 2d, 2e**), also observed in XRD results may be visualized in SEM images. Although the binder structures are generally amorphous, they contain low amounts of needle-formed C-S-H crystals as well (**Figure 2f, 2g**). Discontinuous micro-cracks produced during C-S-H formation are another prominent feature (Tunçoku, 2001).

CONCLUSION

The hydraulicity of the plasters and/or their binders was evaluated based on an analysis program combining mineralogical (acid loss, ignition loss, XRD and petrography) and chemical (SEM-EDS) methods, supported with physical characterization. (Table 2) The results presented here are consistent with those obtained in other research projects on early modern hydraulic binders elsewhere (Pecchioni et al., 2005; Sabbioni et al., 2001; *Decorated Renders*, 1999: 128; Baturayoğlu Yöney, 2008; Baturayoğlu Yöney and Ersen, 2009b).

Some of the plaster matrices were lighter in colour, indicating that fat limes were utilized with artificial pozzolans (02.YC, 06.BR, 11.SP, 12.YR.b, 13.GR.b) or that water limes (03.IC, 05.BR, 13.GR.t, 14.GR , 16.YR.b, 16.YR.m , 18.AR.m, 19.BR) and/or light-coloured natural/artificial cements (12.YR.t, 21.BR.t, 23.GC) were used. The rest of the samples comprising about one half of those that have been studied (01.GR, 04.YR.b, 04.YR.t, 08.BR, 09.BR, 10.BR, 12.YR.t, 15.YR, 17.YR, 18.AR.b, 18.AR.t, 20.BR.b, 20.BR.t, 21.BR.b, 21.BR.m, 22.BR.b, 22.BR.t) are in shades of grey and brown and generally much darker in colour.

Most of the binder matrices are stained with iron oxide in a red-brown colour, probably combined with brick dust, and have evenly distributed matte black ash/cinder/slag dust. Opal, a natural pozzolan was found in two samples (01.GR, 20.BR.t). It is interesting to note that those plasters classified as cements, also have the same pozzolanic additives as the fat and/or water limes. Ashes may have been utilized as a light, fire-resistant aggregate. But the use of traditional artificial pozzolans with hydraulic binders may also indicate distrust in these new construction materials in this period of architectural transition at the turn of the last century.

The broken crystal structure of the matrices in SEM images (at 500x, 1500x, 3500x magnification) is uniform and indeterminate, which is generally true for all types of cement matrices (Odler, 2004, 273**)**. As all of the hydraulic binders, with or without artificial and/or natural pozzolanic additives have similar chemical compositions and therefore form similar compounds during dehydration and setting (Massazza, 2004). Thus, the presence of one or more known cement component alone is not enough to determine the binder type.

Anhydrite calcium silicate, aluminate and aluminoferrite areas, which form the hydraulic bonding, are denser in cements compared to other types of weaker hydraulic binders. These anhydrite compounds have a well-known crystal structure, and belite (C_2S) and alite (C_3S) are more conspicuous. They may be distinguished under polarizing light microscopes (Lawrence, 2004, 146-7; Elsen, 2006; Sabbioni et al., 2001) and SEM images at larger magnification (Odler, 2004, 279; Callebaut et al., 2001). Amongst the analyzed samples, belite was observed in only one case (22.BR.b) in SEM-EDS (**Figure 2f, 2g**) and belite crystals were defined in the thin sections from the same sample (22.BR.b, 22.BR.t) under a polarizing microscope (**Figure 2c**).

Another additive decisive for defining the binder type is gypsum for cements (Baturayoğlu Yöney, 2008; Baturayoğlu Yöney and Ersen, 2009b), which is an additive used to regulate setting since 1850s. Gypsum was observed in 11 samples during XRD and SEM-EDS analyses (**Table 2**). Of these, the gypsum content of which was defined as minute semi-quantitatively (01.GR, 12.YR.t, 15.YR, 18.AR.t, 20.BR.b, 20.BR.t, 21.BR.t, 22.BR.b and 23.GC) probably have cement binders, 20.BR among them being perhaps dated later to the first quarter of the 20th century. Two samples (02.YC and 06.BR) which contained similar amounts of gypsum, on the other hand must have been produced with a fat lime binder and artificial pozzolanic additives as defined through other analyses.

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Anahtar Sözcükler: yapay taş; hidrolik bağlayıcıların gelişimi; erken çimentolar.

GEÇ 19. VE ERKEN 20. YÜZYILDA YAPAY TAŞ MİMARİ KAPLAMA VE ELEMANLARDA KULLANILAN BAĞLAYICI VE AGREGALAR ÜZERİNE BİR DEĞERLENDİRME

'Yapay taş' olarak tanımlanan malzeme, 19. yüzyıl sonu ve 20. yüzyıl başı mimarlığında özellikle dış cephelerde sıklıkla kullanılan, bağlayıcı, agrega ve diğer bazı katkılardan oluşan ve doğrudan yüzeylere uygulanan ya da kalıplara dökülerek hazırlandıktan sonra yüzeylere sabitlenen, bir kaplama ve bezeme malzemesi ve tekniğidir. 19. yüzyılda gerçekleşen Endüstri Devrimi'nin de etkisiyle standartlaşan ve serileşen mimarlık üretimi, gerektirdiği iş gücü ve süre nedeniyle maliyeti yüksek geleneksel

sistemlerden uzaklaşarak, döneminin dinamikleşen sosyal, ekonomik ve kültürel yapısına uygun malzeme ve uygulama yöntemlerinin arayışına girer. Ortaya çıkan çözümlerden biri, pahalı ve yavaş geleneksel taş işçiliği yerine benzer görüntüye sahip, daha hızlı ve seri olarak üretilebilen yapay taş teknolojisidir.

Bu araştırmanın amacı, sözü edilen dönemde yapı dış cephelerinde kullanılan yapay taşları, bunları oluşturan bağlayıcı ve agregaların sınıflamasına dayalı olarak mimarlık ve koruma bilimi açısından değerlendirmektir. Yapı dış cephelerinin mimari, malzeme ve uygulama niteliklerine odaklanan incelemeler sonucu arazi çalışmasında, döneminin özelliklerini yansıtan yapılar seçilerek, yapı dış cephelerinin mimari düzeni içinde yer alan farklı yapay taş uygulamalarından örnekler alınmıştır. Yapay taş başlığı altında farklı sıva teknikleri ile kabartma bezekli mimari elemanlar ele alınmaktadır.

Benzer harç ve sıvalar için literatürde önerilen çalışma programları esas alınarak ilgili ulusal ve uluslararası standartlara uygun olarak gerçekleştirilen deneylerle, temelde hidrolik nitelik taşıyan harçlardan oluşan bu örneklerin fiziksel, hammadde ve mineralojik özellikleri belirlenmiştir.

Elde edilen sonuçlar bağlayıcıların hidrolik niteliğe sahip olduğunu göstermektedir. Bunların bir bölümü yapay olarak üretilmiş çimentolar, diğerleri ise sukireçleri ve/veya opal gibi doğal veya tuğla tozu, kül, odunkömürü, curuf gibi yapay puzolanik katkılı yağlı kireçlerdir. Bazı bağlayıcılarda rastlanan magnezitin ($MgCO_3$), kireç harçlarının mekanik özelliklerini yükselttiği bilinmektedir. 1850'lerden başlayarak bağlayıcının priz süresini düzenlemek amacıyla klinkerin çimentoya dönüştürülmesi sırasında katıldığı bilinen alçıtaşının (kalsiyum sülfat, $CaSO_4.2H_2O$) XRD ve SEM-EDS gibi ileri analiz yöntemleriyle belirlenen varlık ve oranına dayanarak, çimentoların tanımlanması mümkün olmuştur. Yak. %5'den daha yüksek oranda kalsiyum sülfat içeren bağlayıcılar ise, kaynaklarda sıklıkla bahsedilen alçı esaslı bağlayıcı ve/veya çimentolar olarak sınıflandırılmıştır.

Genel fiziksel özellikleri bakımından harç ve betonlardan farklı ve sıvalara daha yakın malzemeler olarak nitelendirilebilecek yapay taşların, yoğunluk ve bağlayıcı/agrega oranları daha yüksek, gözeneklilikleri daha düşük ve agrega boyutları daha küçüktür. Tek tabakalı üretilmiş olabilecekleri gibi iki veya üç tabaka halinde de uygulanabilirler. Beklenebileceği gibi, alt kaba sıva tabakalarıyla karşılaştırıldığında, üst ince sıva tabakalarının yoğunluk ve bağlayıcı/agrega oranlarının daha yüksek, agregalarının daha küçük boyutlu ve beyaz kum, kireçtaşı veya mermer kırığı gibi malzemelerin tercih edilmesi nedeniyle daha açık renkli olduğu söylenebilir. Saman, kıtık gibi lifli agregalar ile puzolanik niteliğe sahip yapay agregalara, hidrolik niteliğe sahip sukireci veya çimento bağlayıcılı olanlar dâhil hemen hemen tüm örneklerde rastlanması, geleneksel uygulamaların, geçiş niteliği taşıyan erken modern dönemde halen devam ettiğini ve uygulayıcıların belki de yeni kullanıma giren hidrolik nitelikli bağlayıcılara güven duymadıklarını düşündürmektedir.

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