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Original article

Mineralogical and microstructural characteristics of historic Roman cement renders from Budapest, Hungary

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ABSTRACT

Roman cements, one of the most extensively produced types of hydraulic binders of the second half of the 19th century, played an important role in the architecture of many European countries. This paper deals with the chemical-mineralogical and microstructural characterisation of historic Roman cement renders from Budapest, Hungary. Different microscopic techniques were used on polished thin sections and fracture surfaces in order to understand the method of producing these renders and the effect of urban pollution on them. The renders exhibited characteristics typical to a Roman cement mortar, such as high binder to aggregate ratios (b/a), mostly fine-grained aggregates and high capillary porosity, but without the shrinkage cracks that are also normally present. This research suggests that coarse residual cement grains may have acted in a manner similar to aggregates by absorbing stress and thereby reducing the formation of shrinkage cracks. Based on the mineral characteristics of residual cement grains, the samples could be divided into two groups, which correspond to either a higher or lower temperature of calcination of the original source material of the cement. Chemical characteristics of the binders suggest the presence of intermixed CaCO_3 originating from the carbonation of hydration products and partly from residual calcium carbonate of the raw material. Despite dense and often impermeable coats applied in later renovations and exposure to a polluted urban environment, which resulted in formation of gypsum on the surface of the renders, the samples show good to excellent state of preservation after more than a century. The strong "house of cards"-like arrangement of the complex C-(A)-S-H-type phases is responsible for both the high capillary porosity and the good resistance of Roman cement renders to atmospheric pollution and potentially damaging salts such as Na- and K-chlorides which are found near the base of the building due to sidewalk de-icing. These results help to better understand the behaviour of historic Roman cement renders, which in turn assists in making good decisions in choosing a repair material to future restorations of 19th century façades built with this material.

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1. Introduction

Roman cement (RC), patented in 1796 by James Parker in England [1] and named because it shared with the lime-pozzolan binder used by the ancient Romans the ability to set hydraulically, took almost half a century to disseminate to the European continent [2]. Most of the Central European countries, such as the Austro-Hungarian Empire, imported small amounts of RC from England before 1850, around when they started their own production, using

local raw materials [3]. One of the earliest Central European applications of RC, based on locally produced binders, took place in 1840 in Pest-Buda (now Budapest). A marlstone from Beocsin/Beočin (in what is today Serbia) was locally burnt by English engineer William Tierney Clark for use in the construction of the piers of the Chain-Bridge crossing the Danube River [4,5]. In the second half of the 19th century, the Austro-Hungarian Empire became the largest producer of RC in Central Europe, where until the end of the 19th century, the major part of the cement production was RC; Portland cement (PC) was a hydraulic binder of secondary importance [5]. At the turn of the 20th century, the production of PC increased rapidly while the importance of RC declined, due in part to a change in style of architecture towards modern functionalism with an absence of ornaments. The more consistent properties of PC due to the standardisation of production technology [2] also played an important role.

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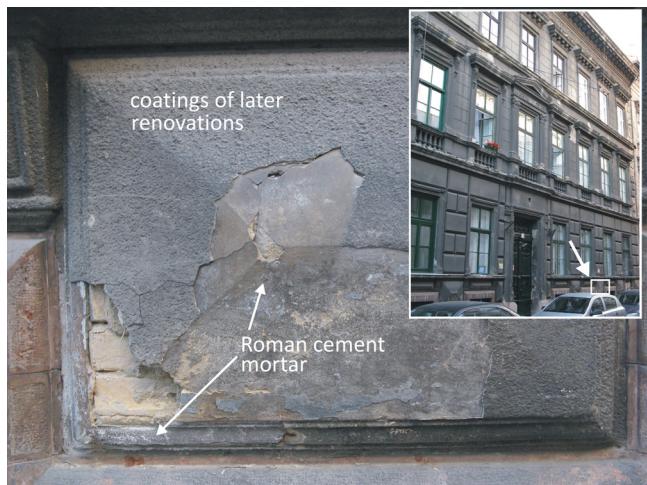


Fig. 1. Characteristic apartment house in the Budapest downtown with slightly damaged diamond-pointed rustication at the plinth made of Roman cement (RC-2).

Roman cement is a highly hydraulic natural cement formed by calcining marls, a fine-grained sedimentary rock that naturally contains carbonate and silicate components in intimate mixture, below the sintering temperature, i.e. between 800 and 1100 °C [2,6,7]. Marls were traditionally burnt in vertical shaft kilns where, due to the low burning temperature, coarse raw feed and large temperature gradients, clinkers with varying degrees of calcination were formed. Based on clinker analyses carried out on a number of historic RC mortars and of systematic calcination tests in laboratory, it is possible to create a RC that is a close match to those created in the 19th century [2,6].

Restoration of historic façades is one of the major tasks in protection of architectural cultural heritage. As a part of the ROCARE project, supported by the 7th Framework Programme of the European Commission, a statistical research aiming at detecting the percentage of 19th century historic buildings in Budapest with façades built of RC renders has been carried out [8]. Being aware of exact historic data regarding the nature and use of RCs in Hungary, the architectural-statistical research has been completed with the material analysis of several historic mortar and render samples. This paper reports a study concerning the chemical-mineralogical composition, microstructure and overall condition of a selection of RC renders. The information gained from this investigation helps to

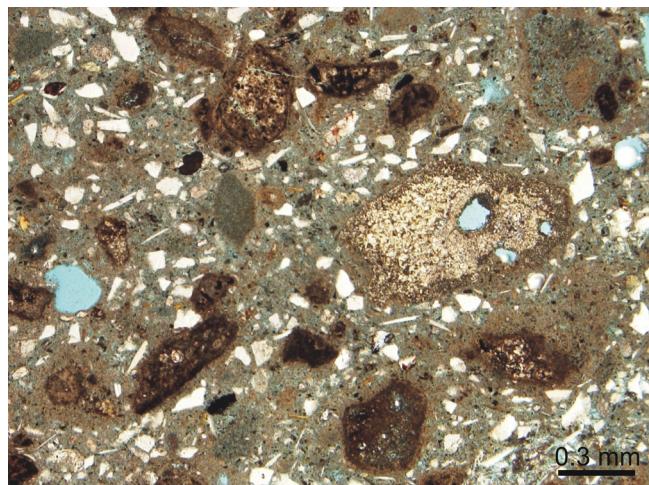


Fig. 3. Sample RC-3: fine-grained aggregates (white) and coarse, differently fired cement grains (slightly overfired with C_2S clusters: center right; optimally fired: dark, surrounded to rounded relics partly with hydration rims: center bottom and top; parallel polars).

better understand the behaviour of historic RC renders and can be used to create a compatible material for use in restoring rendered façades [9,10].

2. Sampling and analytical methods

Seven multi-layered render samples containing the original RC renders along with the layers of later renovation or construction phases (Fig. 1) were taken from the façades of apartment buildings constructed between 1870 and 1912 (Table 1). Polished thin sections were prepared from the samples that had been impregnated under vacuum with a low viscosity epoxy resin dyed blue. They were analysed with optical microscopes (Nikon SMZ 1500, Zeiss AXIOScope A1) using both transmitted bright and dark field as well as incident light. The binder-to-aggregate ratio (b/a) and the grain-size distribution of aggregates and cement remnants were estimated for each sample by using a polarising microscope at magnifications 50–100 \times , by superimposing a square grid and area counting [11]. A scanning electron microscope (SEM, Zeiss EVO MA 15) coupled with an energy dispersive X-ray spectrometer (EDS, Oxford DryCool) was used to make a number of point analyses

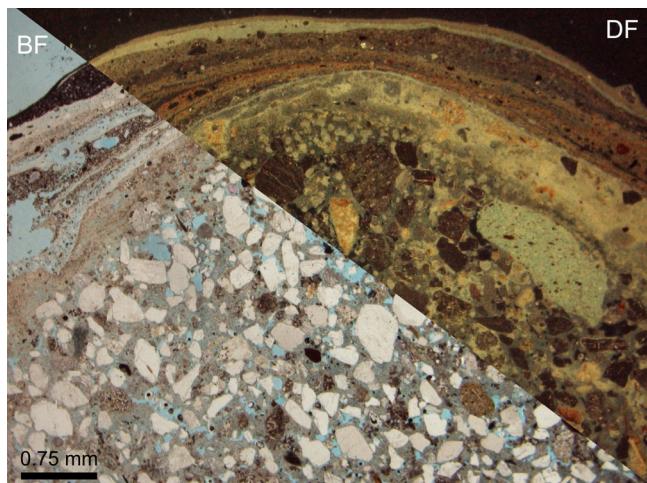


Fig. 2. Roman cement mortar covered with several lime-, PC- and acrylic dispersion-based coatings (RC-1; bright field of view, parallel polars: BF and dark field of view: DF).

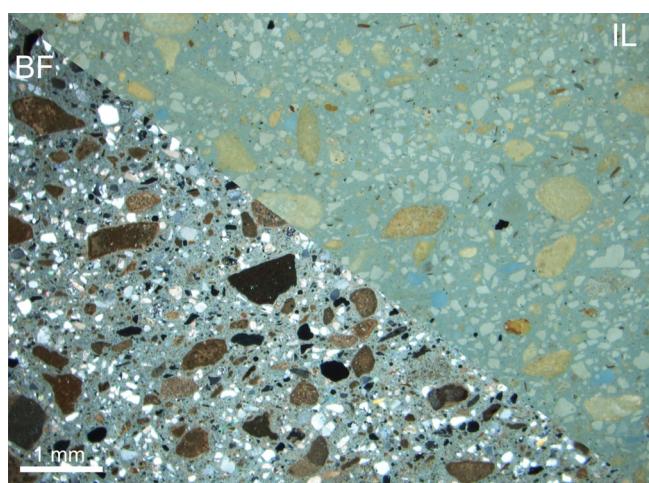


Fig. 4. Coarse residual cement grains (dark and bright brown particles) and fine-grained, well-sorted aggregates (white) in the sample RC-6 (bright field of view, crossed polars: BF; incident light: IL).

Table 1
Description of the sampling sites.

Nr.	Location (district, street)	Date	Sampling site
RC-1	5th, Vadász 20	1871	Door casing, ground floor
RC-2	5th, Vadász 32	~1870	Diamond-pointed rustication, plinth
RC-3	5th, Báthory 16	1891–92	Channel-jointed rustication, plinth
RC-4	6th, Vasvári Pál 9	1896	Window casing, ground floor
RC-5	6th, corner Hajós 19 – Dessewffy 10	1895	String course between rusticated surfaces, ground floor
RC-6	6th, Hajós 16–18	1912	Plane rustication, plinth
RC-7	13th, Szt. István 22	~1885	Rusticated column, ground floor

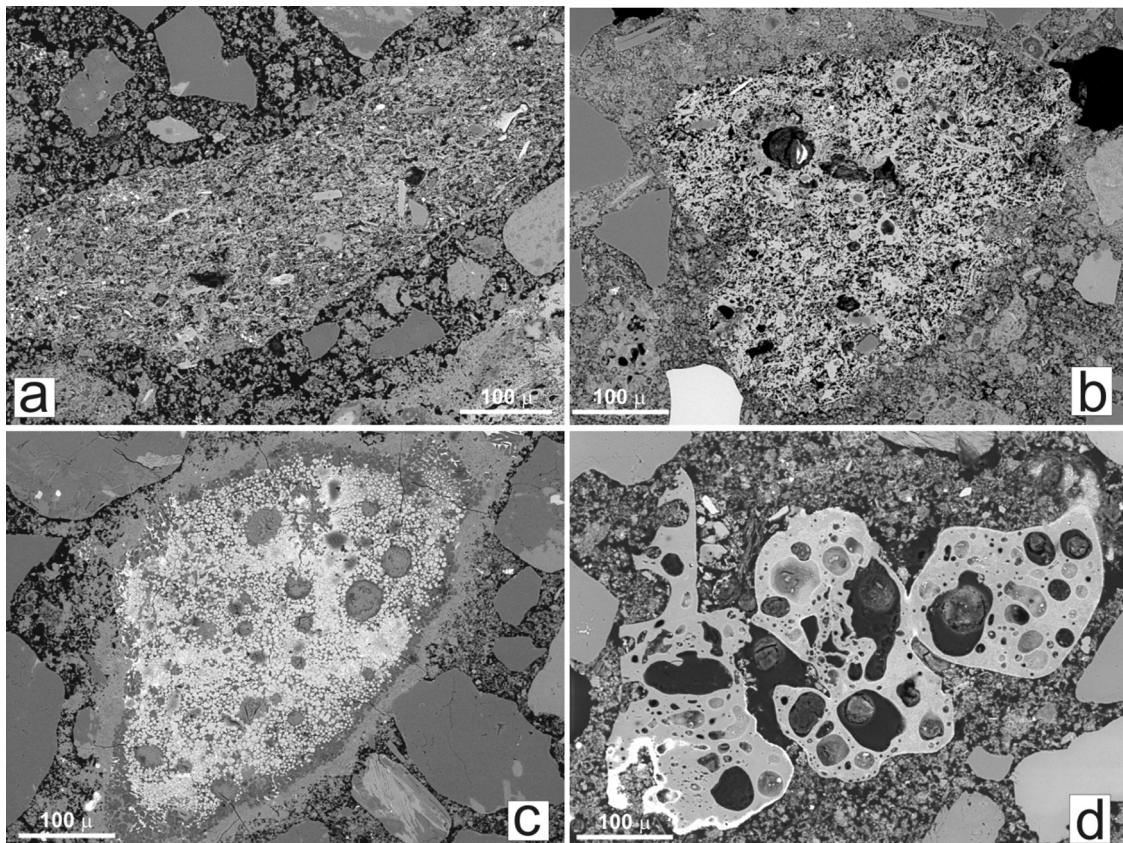


Fig. 5. Characteristic residual cement grain types of RC binders (Table 3): a: underfired with remnants of quartz, carbonate and mica; b: optimally fired with Ca-diffusion rims around silicates and C₂S; c: optimally fired with large amounts of C₂S, interstitial Ca-Al-ferrite phases and dense, partly carbonated hydration rims; d: overfired with glassy structure and large air voids caused by local melting; SEM-BSE.

to characterise the chemical composition of the hydraulic phases and the binders of samples. Fracture surfaces of the mortars were sputtered with gold and investigated in high vacuum with a field emission scanning electron microscope (FEI, Quanta 200).

3. Results and discussion

3.1. Characteristics of aggregates

The petrographic characteristics of the mortars have been summarised in Table 2. All samples contain moderately to well-sorted, angular to rounded aggregates of a wide range of different silicate and carbonate minerals as well as rock fragments suggesting their fluvial origin. With the exception of the sample RC-1 (Fig. 2), observations refer to the use of fine- to medium-grained sands (Figs. 3 and 4). The estimated b/a ratios (Table 2) vary between 1:1 and 2.5:1; a high proportion of binder to aggregate is typical for historic RC mortars [12]. Although historic Roman cements renders often exhibit a characteristic pattern of shrinkage cracks [13], because of the low amount of aggregates, shrinkage

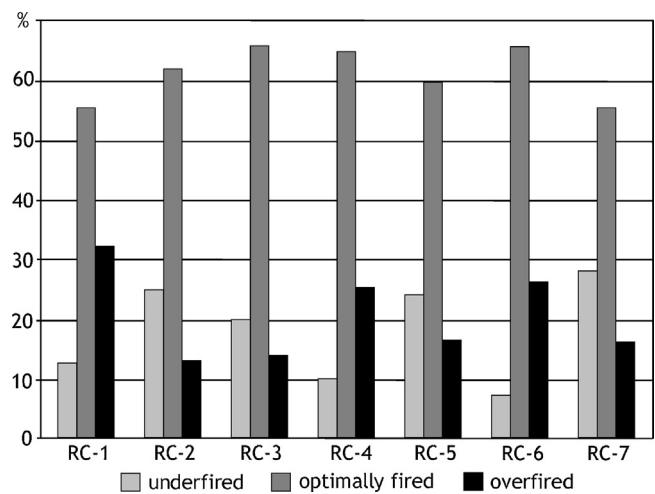


Fig. 6. Classification of the binders based on the content of their residual cement grain types.

Table 2

Petrographic characteristics of the samples.

Sample	Average/maximum grain size of cement grains	Average/maximum grain size of aggregates	Type and estimated amount of aggregates	Sorting of aggregates	Estimated b/a ratio
RC-1	200 to 400/700 µm	300 to 500/1500 µm	Q > polyQ > cc. > met. > fp&plag. > plut. > volc. > sed. > mi. + ch.ree.	Moderate	1
RC-2	300 to 600/800 µm	100 to 200/700 µm	Q > polyQ > plut. > volc. > met. > sed. > fp&plag.-mi.	Good	2
RC-3	400 to 800/1000 µm	100 to 200/600 µm	Q > polyQ > cc. > fp&plag. > sed. > plut. > mi.	Good	2
RC-4	200 to 400/500 µm	50 to 100/300 µm	Q > polyQ > mi. > cc. > fp&plag. > sed. > plut.	Good	2
RC-5	200 to 400/600 µm	100 to 200/500 µm	Q > polyQ > mi. > cc. > fp&plag. > sed. > plut. + ch.ree.	Moderate	1.5
RC-6	400 to 600/700 µm	100 to 200/800 µm	Q > sed. > polyQ > cc. > plut. > volc. > fp&plag. > met.	Moderate	1.5
RC-7	100 to 300/400 µm	200 to 300/1500 µm	Q > polyQ > fp&plag. > cc. > met > plut. > volc. > sed. > mi.	Good	1.5

Q: monocrystalline quartz; polyQ: polycrystalline quartz; fp&plag.: K-feldspar and plagioclase; cc.: calcite + limestone; mi.: mica; sed.: sedimentary rock fragment; plut.: plutonic rock fragment; volc.: volcanic rock fragment; met.: metamorphic rock fragment; ch.ree.: chopped reed.

cracks could only be occasionally found in the render samples; most samples being free of them (Figs. 2 and 4).

3.2. Optical and mineral characteristics of residual cement grains

The most characteristic feature of the historic RC renders samples is an inhomogeneous structure of their binders which are up to 25% comprised of distinct, coarse residual cement grains [2], also called phenograins [14], which can exhibit a diameter of up to 1 mm (Figs. 3 and 4). The reason for the broad grain-size distribution of historic RCs is due to coarse milling, the ability to mill cement clinker to the fineness that ball mills used in the production of Portland cement production did not exist until the turn of the 20th century [15].

Due to the significant presence of a grain-size fraction in the range of 200 to 400 µm, residual cement grains may exceed the aggregates in average size (Table 2) which holds for all but two samples (RC-1 (Fig. 2) and RC-7). The above observation helps to understand why, despite the high b/a ratios and the usually dense matrix, shrinkage cracks have developed only exceptionally: the cement remnants have acted similarly to fillers and aggregates by absorbing stresses [2,12,16]. Furthermore, hydration rims have caused a strong chemical bond between the coarse cement grains and the matrix.

In order to characterise the cements, approximately 100 residual cement grains ranging from 0.1 to 1 mm in diameter were analysed and statistically evaluated in each sample. They exhibit different microstructures and mineral compositions which can be attributed

to whether each grain was optimally fired or under- or overfired [17–19] (Fig. 5, Table 3). In all samples, the optimally fired cement grains dominate (56 to 66%), while the percentage of under- and overfired types varies between 8 and 28% and 12 and 32%, respectively. In this way, the mortar samples can be grouped into two types based on the ratio of under- to overfired cement particles (Fig. 6). One group (RC-1, 4 and 6) contains samples with a larger amount of overfired grains and the other group (RC-2, 3, 5 and 7) contains a larger amount of underfired cement grains. The high amount of optimally fired residual cement present in both groups points to the possible pre-selection of optimally fired clinker before grinding: a procedure well known to be used during the historic Roman cement times [3].

Furthermore, since Central European historic RCs were free of C₃S and of C₃A [18], their extraordinary short setting times were caused by the hydration of amorphous Ca-aluminates linked to the formation of various AFm phases [20,21]. The amorphous portion of a RC decreases at temperatures above about 900 °C, the supposed higher degree of calcination indicated by the predominance of overfired cement grains may have brought about a retarded set of the mortars during hydration [18]. The results suggest that different batches of cements may have influenced the workability of the mortars. Thus, due to the decrease in amount of highly reactive clinker constituents at elevated temperatures [6], samples containing larger amount of overfired components suggest slower setting, while mortars containing significantly lower amount of overfired cement phases may have yielded shorter setting times of the mixture [18].

Table 3

Optical characteristics and mineral composition of residual cement grains in Central European Roman cements. Nomenclature based on [16,19].

Type	Optical characteristics	Characteristic mineral composition
Underfired (sub-optimal)	Subangular to subrounded Original texture of raw material (marlstone) still recognisable Sometimes thin hydration rim	Quartz, mica, feldspar, calcite (remnants of microfossils) Silicate grains with thin Ca-diffusion rims
Optimally fired (optimal)	Subangular to rounded grains Zoned silicate (Q, Kfp) grains with Ca-diffusion rims Fibrous or fully-hydrated, dense matrix Dense, partly carbonated hydration rim	S (C) CS C ₂ S C ₃ S ₂
Optimally fired (super-optimal)	Clusters of C ₂ S Coarse pores With abundant local melting Dense, partly carbonated hydration rim	C ₂ S Ca-Al-ferrite phases CS C ₂ AS
Overfired (super-optimal)	Subrounded to very angular Coarse crystalline Graphic intergrowth texture Local melting Rarely with a thin hydration rim, but usually acts inert	C ₂ AS Ca-Al-ferrite phases Glass (C ₂ S, CS)

S: SiO₂; C: CaO; CS: wollastonite; C₂S: belite; C₃S₂: rankinite; C₂AS: gehlenite.

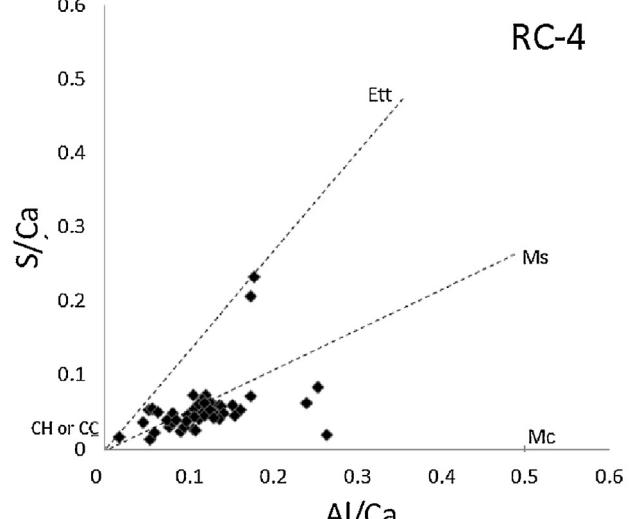
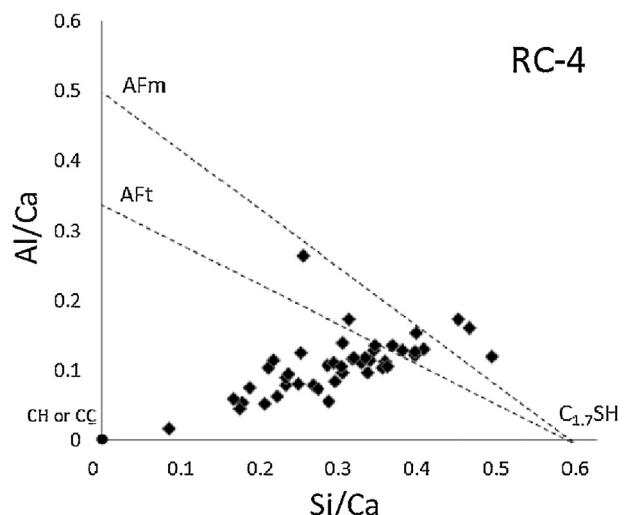
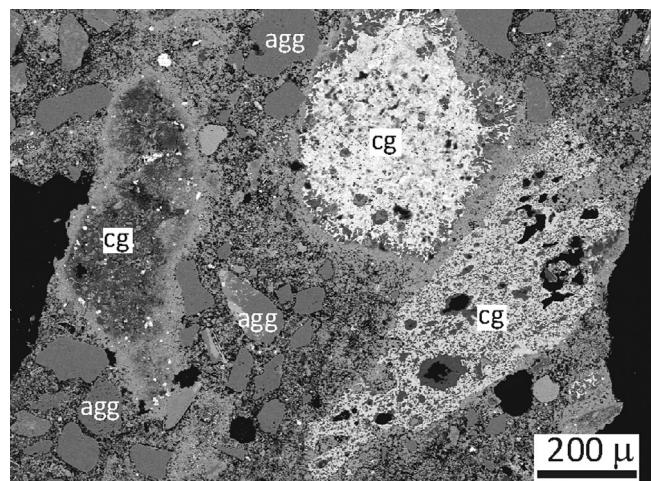
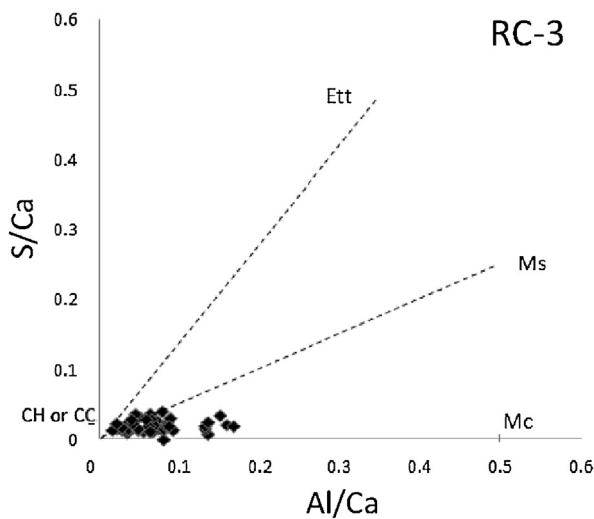
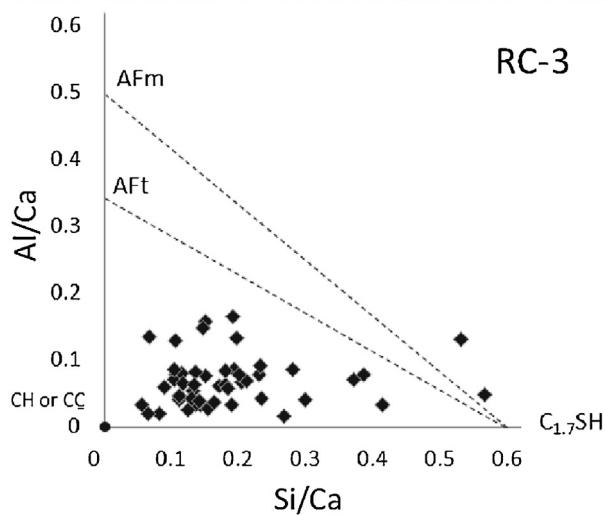
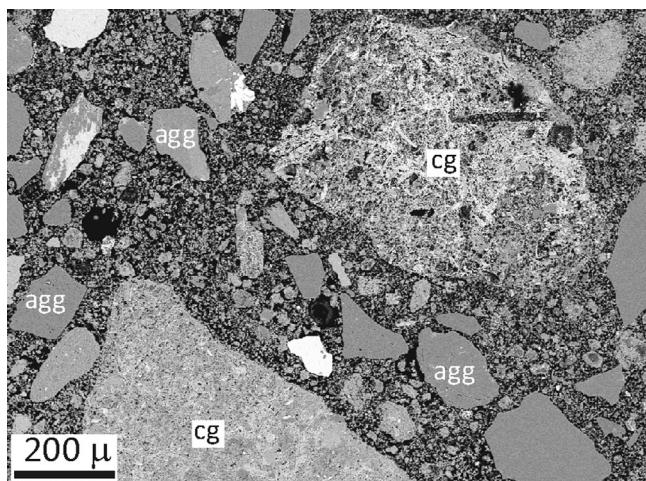


Fig. 7. Chemical characteristics of the binder of the sample RC-3 (cg: cement grain, agg: aggregate).

3.3. Optical and chemical characteristics of binders

The hydrate matrix of the samples reveals a typical anisotropic, but inhomogeneous appearance caused partly by the carbonation of hydrate phases and partly by a small amount of excess free lime and/or not fully decomposed calcium carbonate [2]. Furthermore, the bluish colour of the binders caused by blue-dyed epoxy resin

Fig. 8. Chemical characteristics of the binders of the samples RC-4 (cg: cement grain, agg: aggregate).

(Fig. 4) indicates a high capillary porosity [13]. Spherical entrained air voids between 0.2 and 0.8 μm in diameter are common in the samples. Large (0.5 to 2 mm) irregular voids (Fig. 4) are a result of air entrapment during the mixing process [22].

Two samples (RC-3 and 4), classified as optimally and slightly overfired cement types (Fig. 6), have been selected to determine the elemental composition (Ca, Al, Si, S, expressed in the atomic ratio

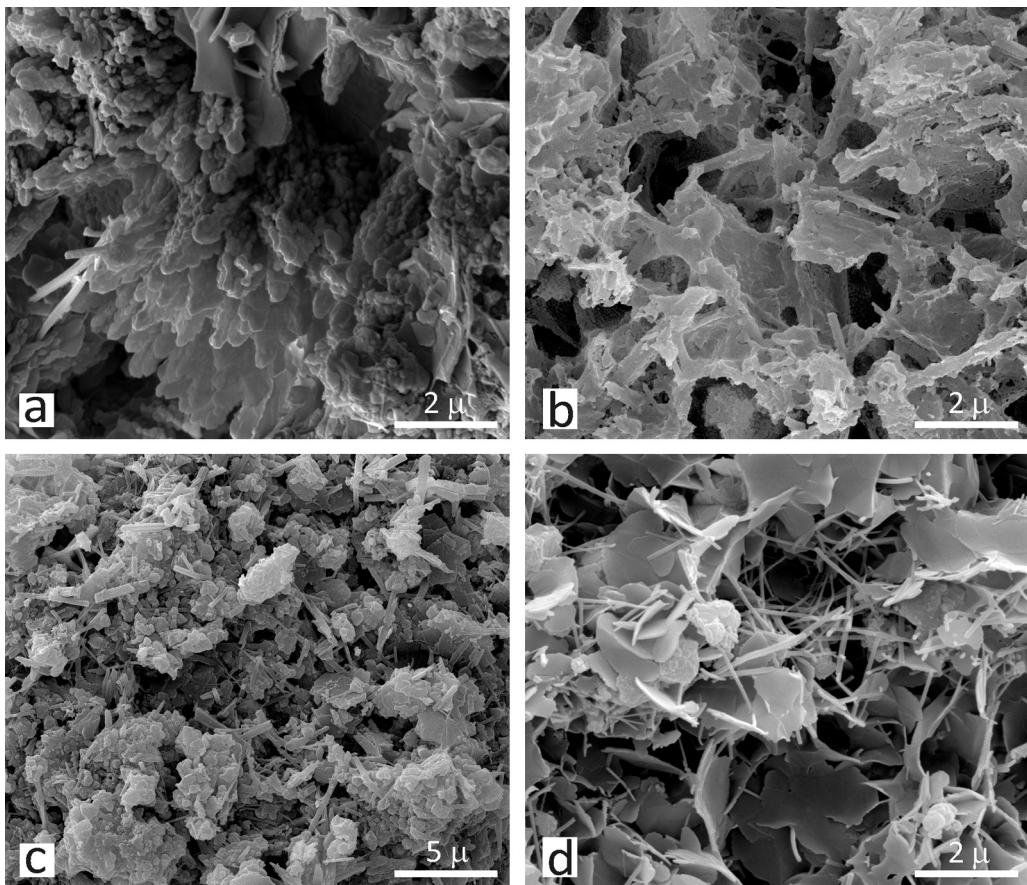


Fig. 9. “House of cards”-like arrangement of partly carbonated C-(A)-S-H phases with high capillary porosity (a–c); RC-4, -5 and -6 (d): 2-days microstructure of an uncarbonated laboratory cement, ROCARE project [27], SEM-SE.

plots) of the hydration products [25]. Sample RC-3 (Fig. 7) exhibits a poorly dense hydrated binder matrix and cement grains that are predominantly without well-developed hydration rims. The Si/Ca and Al/Ca ratios plot in the range of 0.1 to 0.2 and 0.05 to 0.2, respectively, and are low compared to those measured in modern RC pastes [23]. The values indicate either carbonation, and/or are they due to remnants of finely dispersed CaCO_3 that has not fully calcined during the firing of the marl. High birefringence of the binder and several unreacted calcite inclusions observed in the optical microscope, support this assumption. Similarly to recent studies on RCs [24], the distribution of Si, Al and Ca suggests that an amorphous C-(A)-S-H type phase, where (A) refers to possible substitution of alumina in the Ca-silicate-hydrate, intermixed with calcium carbonate dominates in the matrix [23]. There is thus no clear evidence of a pure end member C-S-H [23]. The Al/Ca vs. S/Ca atomic ratio plot clearly shows that the hydration products do not contain any sulphur-bearing phases.

In the Si/Ca vs. Al/Ca plot of the sample RC-4 (Fig. 8), a more clearly linear trend with a lower spread of values can be observed, which again refers to the presence of a C-(A)-S type hydrate phase partly intermixed with CaCO_3 as a product of carbonation. This coincides with the observation that C_2S crystals are often depleted in Ca on their margins and transformed into hydrous silica grains; a process also linked to carbonation [25,26]. On the contrary to RC-3, the Al/Ca vs. S/Ca plot shows that the matrix contains SO_3 -bearing hydrate phases. Based on the atomic ratio plot (Fig. 8) it may be attributed to ettringite precipitated in the matrix. Since ettringite is not stable in low alkaline environments (i.e. pH < 9) [27], it has probably persisted because carbonation is only partial. As confirmed by the optical analysis, in the sample neither secondary ettringite (e.g.

in the form of pore-fillings), nor the effect of sulphation on its surface could be observed. The amount of sulphate-bearing hydrate phases can thus be considered as negligible and suggests probably a cement batch produced either from a SO_3 -bearing marlstone [9] and/or using a sulphur-rich fuel.

3.4. Microstructure of the binders and secondary salt efflorescence

Recent studies [2,12] have shown that historic RC mortars usually have remarkably high compression strengths up to 50 to 60 N/mm² and, at the same time, a high capillary porosity. Investigations [2,12,28] on microstructures have revealed that a typical RC mortar, whether historic (Fig. 9a–c) or newly produced (Fig. 9d), is characterised by a high porosity formed by coarse C-(A)-S-H type products [23] of predominantly platy shapes with “house of cards”-like arrangement. This structure is clearly responsible for the coincidence of high mechanical strength with high capillary porosity.

Each sample in this study featured the typical “house of cards”-like structures described above, yet some differences could also be observed. The platelets are often covered with 0.1 to 2 μm large spherical or cauliflower-shaped to rhomboidal crystals (Fig. 9a–c), referring to the presence of calcium carbonate polymorphs such as vaterite, aragonite or calcite as carbonation products of the hydrate phases [29]. Comparing the microstructure of the historic samples to those of a 2-days laboratory RC (Fig. 9d), no traces of carbonation of the platy hydrate phases were detected in the young paste [27]. A predominant size of pores, located between the hydrate platelets, is in the range of 1 to 5 μm in diameter, thus they belong to the range

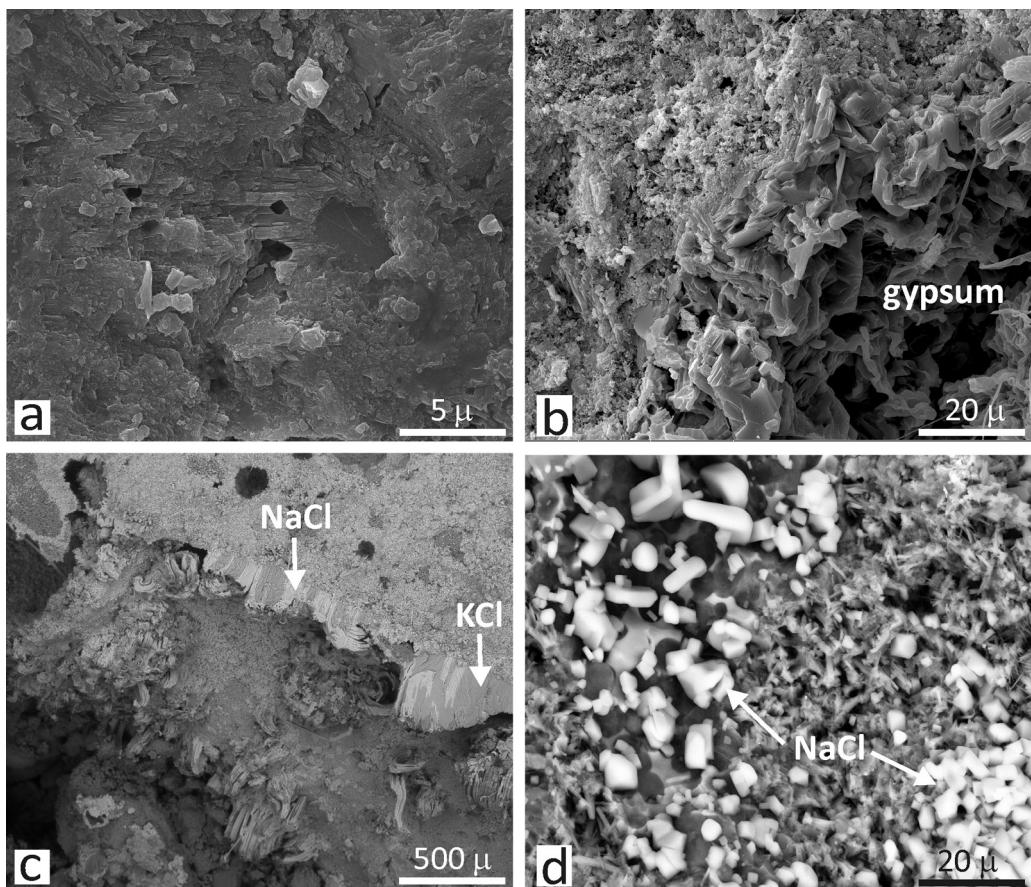


Fig. 10. Formation of massive (a, RC-7) and idiomorphic (b, RC-6) gypsum crystals (SEM-SE) as well as NaCl and KCl whiskers as fillings of large air void (c) and homogenously distributed, idiomorphic NaCl crystals in the subsurface capillary pores (d); RC-2, SEM-BSE.

of capillary pores as suggested by the optical microscopy. Based on observations carried out on test cements produced in a laboratory, the highly porous, “house of cards”-like structure was typical for early or intermediate stages of hydration [28].

The formation of massive (Fig. 10a) or idiomorphic gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystals (Fig. 10b) could be detected in the subsurface zones of the matrices, up to a depth of app. 1 mm, in the samples RC-1, 3, 5, 6, and 7. The formation of gypsum is a result of a chemical reaction between primary and secondary carbonate components of the binder and atmospheric SO_3 . Large amount of halite (NaCl) originating from de-icing salts in the urban environment were found in the form of whiskers and xenomorphic to hypidiomorphic crystals (samples RC-2 and 3), either as fillings in large air voids (Fig. 10c) or as very fine-grained crystals homogenously distributed in the matrix (Fig. 10d). Sample RC-2 also contains small amounts of sylvite, KCl (Fig. 10c). Because of high capillary activity, salt solutions could be easily transported to the surface or to the boundary of later paint layers with lower permeability where the efflorescence often took place. Thus, formation of secondary cracks subparallel to the surface due to salt efflorescence could exceptionally be detected between the original RC render surfaces and coatings and not in the RC mortars.

3.5. Finishing coats

Thin dark dust horizons on the surfaces of the RC renders refer are evidence that the original surfaces were uncoated. The mortar samples RC-1, -4 and -5 were additionally coated using RC-finishing washes. All samples were covered with a typical, but variable sequence of lime-, PC- and/or lime-PC-based coatings as well as

acrylic dispersion paints of variable thickness (Fig. 5). The paint layers of the earlier restoration campaigns, often exhibiting gypsum as a product of atmospheric pollution, were frequently pigmented with red or yellow ochre, showing attempts to regain the original colour of the polluted façade. In contrast, the later PC-based as well as the acrylic dispersions were rather greyish in colour, containing often deliberately by-mixed unidentified organic pigments and/or dust particles. Aim of this procedure was to match the dark colour of corroded surfaces; a method frequently used for creating a homogenous look of entire façades in Budapest's polluted downtown during the 20th century.

4. Conclusions

This study has discussed the mineralogical characteristics and microstructure of some 19th century Roman cement renders from Budapest, Hungary observed by various types of microscopic methods. Although all samples have been taken from façades of apartment buildings situated in the most polluted districts of the city, they appeared to be well preserved, an observation which supports the long-term durability of mortars made from Roman cement binders. Specific petrophysical characteristics, such as high binder-to-aggregate ratios, well-sorted and fine-grained aggregates, the absence of shrinkage cracks, high capillary porosity, and the large amount of coarse cement grains are evidence of a quite unusual way of manufacturing, preparing and applying these hydraulic mortars, and shed some light on their historic performance as durable building materials. Especially conspicuous in this context was the large average grain size of the residual cement grains relative to the average grain size of the aggregates

in most samples. These residual cement grains, partially adopting the functions of aggregates, could participate in averting the formation of shrinkage cracks and thus contributing to developing sufficient mechanical strength. The binders of the mortars studied here represent two different types of Roman cement with different proportions of cement components formed at either lower and higher firing temperatures. The composition of the cements may also have influenced the early strength development of the mortars, especially the speed of set. The chemical composition of some of the binders suggests a complex matrix of C-(A)-S-H-type nature partly intermixed with CaCO_3 that is present as a product of carbonation and/or from unreacted carbonate components in the raw material. Traces of salt crystallisation in the form of sulphation and efflorescence of chlorides can be found in most samples, yet their effects have been mainly restricted to the surface of the renders due to their high macro-porosity. Large voids of entrapped air acted as reservoirs for salt crystallisation in some samples while the cement hydrate matrix maintained sufficient durability. These properties explain the durable nature of historic Roman cement renders against salt and atmospheric weathering processes and recommend their potential use as restoration materials for buildings that are part of the architectural heritage of the 19th century.

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