Brick-Lime Mortars and Plasters of a Sixteenth Century Ottoman Bath from Budapest, Hungary

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> *I have explained how plastering is executed in dry situations; now I shall give directions for it, that it may be durable in those that are damp. [. . .] The wall is then to be plastered with the potsherd mortar, made smooth, and then polished with the last coat.*
> *Vitruvius (Ten books on architecture)*

1 Introduction

There are two ways to obtain mortar and plaster binders that can harden under water. Both procedures lead to similar products, i.e. compounds of Ca with Si, Al and Fe, capable of binding water molecules in their solid structure.

1.1 The Pozzolanic Principle

The admixture of reactive siliceous compounds such as volcanic tuff or crushed bricks, the so-called "pozzolanas", to slaked lime produces hydrate compounds.

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Such mortars can not only be set under water, but are also water-resistant and develop higher mechanical strength than air-hardened lime mortars. The ancient Greeks and especially the Romans developed this technique to a high level, which enabled them to construct aqueducts, bridges and bath buildings, and even to cast large elements in a manner similar to the modern concrete technology. The use of crushed or finely ground bricks, called *Horasan* in present day Turkey, or *cocciopesto* in the Roman Empire, continued in Byzantine times, and survived during the Ottoman Empire in the construction of several buildings, among which thermal baths.

1.2 The Hydraulic Principle

At the end of the eighteenth century, a major change occurred in producing binders with hydraulic properties. The calcination of limestone contaminated with clay (natural hydraulic lime), or of marlstones (natural cements), produces Ca-silicate and Ca-aluminate phases that can react with water, producing mortars with increased mechanical strength and durability. From the second half of the nineteenth century onward, the development of this technology made possible the production of modern Portland cements burned at high temperatures.

When impure limestone or marlstone containing silica and clay are burned at temperatures between 800 and 900°C, the clay decomposes and reacts with the lime, forming calcium silicates and aluminates. The maximum burning temperatures for natural hydraulic limes and Roman cement is 1,250°C. Modern Portland cement is produced from mixtures of limestone and clay burned in the range of 1,400°C, a temperature at which sintering occurs and a clinker is formed.

Between 1526 and 1686, part of the Hungarian Kingdom was occupied by the Ottoman Empire. During this period, several buildings, among which thermal baths, were constructed. One of the largest Ottoman baths in Budapest, the Császár (Emperor) Bath (Fig. 1a) was built in 1574 by Sokollu Mustafa and rebuilt several times during the last centuries. In recent years, a modern renovation of the structure has begun, including aspects of art historical research aimed at reconstructing the original Ottoman colouring of the interior of the building. The archaeometric study of plasters and mortars represents part of this interdisciplinary cooperation. Ottoman brick-lime plasters and mortars of different colours (white, pink, and red) were identified in the interior of the Bath (Fig. 1b). The determination of their physical, mineralogical and microstructural characteristics and the assessment of their pozzolanic and hydraulic properties are essential for understanding the motives for using brick-lime mixtures as plasters and mortars in this building. In this study we present some preliminary results of material characterization carried out by polarizing and scanning electron microscopy, as well as X-ray diffractometry (XRD).

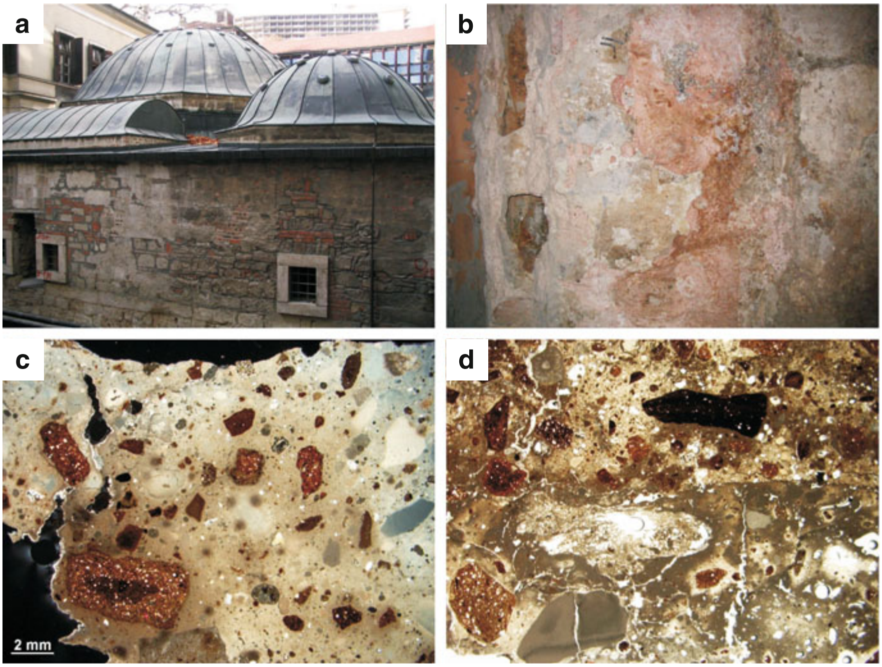

Fig. 1 (**a**) The Császár Bath in Budapest, Hungary. (**b**) Ottoman brick-lime plaster fragments in the Császár Bath. (**c**) Microscopic image of white brick-lime mortar (+N). (**d**) Microscopic image of pink (*bottom*) and red (*upper part*) brick-lime plaster (1N, width of image: 8 mm)

2 Results

2.1 Polarizing Microscopy

Microscopic analyses showed that in all three colour types the binder seems to be microcrystalline calcite; however, with an atypical low birefringence, cloudy structures, and dense texture around the brick fragments (Fig. 1c, d). The amount of inert aggregates, i.e. sand, is very low; only some small quantities of quartz and feldspar clasts were observed. Very fine-grained brick dust, together with larger brick fragments up to 3–4 mm in diameter, represents the pozzolanic additive in the samples. The admixed brick fragments are red to reddish brown in colour, with identifiable mica, quartz, and feldspar grains. Some larger brick fragments exhibit darker or lighter reaction rims (Fig. 1c, d). Partly zoned, fine-grained, binder-related particles, the so-called "lime lumps" (Hughes et al. 2001), with irregularly low birefringence were also observed in all samples. The reddish type plasters are cracked perpendicularly to the surface, and cracks and pores are often filled with secondary sparitic calcite (Fig. 1c, d).

2.2 X-Ray Diffractometry

Calcite, quartz, K-feldspar, plagioclase and phyllosilicates (sericite–illite, chlorite, sometimes kaolinite) are the main phases of the plaster and mortar samples. Hematite was mainly identified in pink and red material. Some samples contained additional components, such as diopside, gypsum, aragonite and vaterite. After dissolving the carbonate content of the samples with dilute hydrochloric acid, the relative amount of silicates has increased, and the presence of an amorphous phase can be assumed due to the elevated baseline of the XRD profile, between 15° and 30° 2θ.

2.3 Scanning Electron Microscopy

The average chemical composition of the "limy" matrix (Fig. 2a) measured by SEM–EDX is ca. 70–80% CaO and 20–30% SiO_2. Most of the brick pebbles exhibited Ca-enrichment in their outer zones. Around them, at the brick-lime interface, compact zones of up to 0.1 mm thickness were observed, predominantly

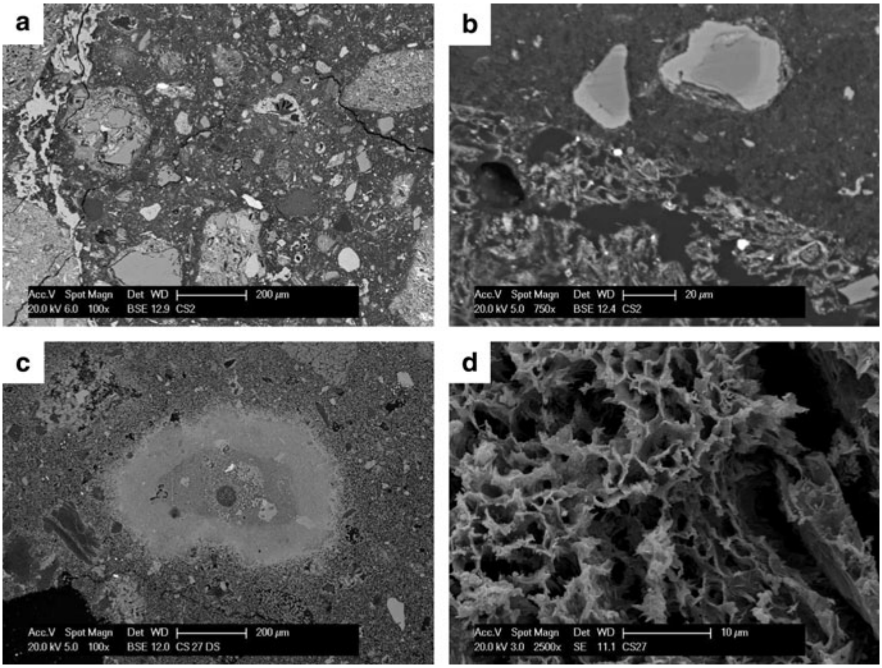

Fig. 2 SEM–BSE images of a red plaster. (**a**) Brick fragments and Si-rich matrix. (**b**) Quartz grains with clear Ca diffusion rims. (**c**) "Lime lump" with Si-rich core. (**d**) Ca- and Si-rich card-house structure of the matrix

composed of Ca with a slight amount of Si and Al. Monocrystalline quartz and feldspar grains with typical Ca diffusion margins were also detected in the matrix (Fig. 2b). Several "lime lumps" showed a typical zoned appearance: their outer rim was rich in Ca, while their inner zones were rich in Si (Fig. 2c).

The SEM-SE observations carried out on broken surface samples showed that the microstructure of the matrix consists of 1–5 μm long needles and plates; sometimes, a so-called "card-house network" of probably amorphous calcium-silicate-hydrate (CSH) phases could be observed (Fig. 2d).

3 Discussion and Conclusions

Based on the macroscopic and microscopic observations, the white and pinkish-reddish plaster and mortar samples from the Ottoman Császár Bath in Budapest seem to be brick-lime mixtures commonly used during Ottoman times for several water-resistant building constructions (Baronia et al. 1997; Böke et al. 2006). Especially in the pinkish-reddish samples, high amounts of brick fragments and dust can be found as pozzolanic additives. The Ca (i.e. calcium-carbonate) enrichment of the matrix in the immediate surrounding of brick pebbles found in several cases does not, however, clearly refer to the presence of abundant calcium-silicate-hydrate (CSH) phases at the brick-matrix interfaces, which are typical for brick-lime mortars (Baronia et al. 1997; Böke et al. 2006; Moropoulou et al. 2002, etc.).

However, the microscopic appearance of the "micritic" groundmass suggests that the binder was probably not composed exclusively of pure $CaCO_3$. This optical microscopic observation is supported by scanning electron microscopy analyses showing relatively high (20–30%) and generally homogeneously distributed Si content in the $CaCO_3$ matrix, which may suggest a relatively good hydraulicity of the materials. The large amount of amorphous material detected by XRD can be derived from the brick aggregates (Böke et al. 2006), but may also refer to the presence of amorphous CSH phases in the matrix. The latter hypothesis can also be supported by the card-house and irregular needle-like structure of the binding material; these structures seem to be unusual for brick-lime plasters and mortars, but were found in nineteenth century natural (Roman) cements (Weber 2007).

Quartz and K-feldspar grains with a Ca-rich rim show inward diffusion of calcium; this phenomenon was also identified in natural cements (Weber et al. 2007), and may refer to the presence of silicate impurities that react with the calcite in the raw material during the lime burning process. The presence of zoned "lime lumps" that contain a certain amount of Si (plus minor quantities of Al and Mg) in their cores also suggests a lime with hydraulic properties, most probably originating from the calcination of impure limestone (Elsen et al. 2004; Zamba et al. 2007).

Preliminary results suggest that the Ottoman mortars and plasters of the Császár Bath may have received their good hydraulic properties not only due to the partly pozzolanic brick additives, but additionally through the formation of new phases with hydraulic properties during the firing of the impure carbonate raw material.

Such potential raw materials (i.e. clayey limestones and marlstones) are widespread on the Buda Hills in the vicinity of the Császár Bath (Wein 1977). Similar brick-lime mortars made from marly limestones or limestone–clay mixtures were found by Moropoulou et al. (2002) in Hagia Sophia (Istanbul).

The precipitation of secondary coarse calcite in cracks and voids, as well as the presence of aragonite in the mortars and plasters, can be explained by the flow of thermal water containing a high amount of dissolved carbonates (Leél-Őssy 1995). Further studies are planned, with the purpose of delineating the effects of thermal waters on the brick-lime materials of the Bath.

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