16th CENTURY HYDRAULIC MORTARS FROM THE OTTOMAN RÁC BATH IN BUDAPEST, HUNGARY

Farkas Pintér[1], Szabolcs Csányi[2], Johannes Weber[3], Bernadett Bajnóczi[4], Mária Tóth[4]

[1]Scientific Laboratory, Federal Office for the Protection of Monuments, Arsenal 15/4, A-1030 Vienna, farkas.pinter@bda.at
[2]Full Design Ltd., Hattyú u. 9., H-1015 Budapest, csanyiszabolcs@t-online.hu
[3]Institute of Art and Technology - Conservation Sciences, University of Applied Arts Vienna, Salzgries 14/1, A-1010, johannes.weber@uni-ak.ac.at
[4]Institute for Geochemical Research, Hungarian Academy of Sciences, Budaörsi út 45., H-1112 Budapest, bajnoczi@geochem.hu, totyi@geochem.hu

Budapest, the capital of Hungary, known as "The city of spas", exhibits a unique geological setting which has allowed constructing thermal baths for 2000 years. Between 1526 and 1686, part of the Hungarian Kingdom was occupied by the Ottoman Empire. The first Ottoman Turkish bath in Budapest was the Rác Bath built in the second half of the 16th century. Between the 18th and 20th centuries the building has been several times extended, so that the simple bath building became a complex. In the recent years, renovation of the object was started, including archaeological and art historical research and restoration activities. In the course of restoration, next to well-known common lime and brick-lime mortars and plasters, in the Ottoman central part of the bath a surprisingly hard, white, fine-grained masonry mortar was found, exhibiting presumably good hydraulic properties and excellent bond to the bricks and stone blocks. The aim of this study was to determine composition, structure, and production technology of this material, using optical and scanning electron microscopy as well as X-ray diffraction analysis. The results can help to better understand the historic techniques; furthermore it may support the restorers' and conservators' choice of suitable mortars for restoration of the monument.

The irregularly low birefringence, dense appearance and small, sharp, "porcelain-like" cracks of the mortar matrix correspond well with its high content of Si along with relatively low amounts of Al as proved by SEM-EDX measurements. Analysis of broken samples indicates that the binder consists of carbonate intimately mixed with a fibrous Ca-silicate phase. The latter one, being most probably a CSH phase, constitutes the hydraulic component in the matrix and explains its uncommon optical behaviour. Presence of tobermorite in the mortar, the occurrence of which is frequently described in historic mortars of hydraulic or pozzolanic nature, was proved by XRD analysis.

The optical properties as well as the chemical and mineralogical composition of white, rounded, binder-related inclusions which are of the same appearance as the well-known lime lumps in historic mortars closely match the bulk of the matrix. Both are therefore believed to reflect the composition of the raw material used for preparing the mortar.

The hydraulic nature of the mortars is not only exhibited by the groundmass, but also by what could be assumed to form the aggregates. Relicts of hydraulic phases containing Ca-silicates, such as e.g. belite, wollastonite and gehlenite as well as a probably a non-stoichiometric Ca-Si-(Al)-ferrite phase, reflect the kiln reactions occurred between silicates and carbonates during the calcination of the raw material. These relicts also exhibit a dense, outer rim with Ca:Si ratios of roughly 1:1 related to the presence of hydrate phases. The relatively low Al content of the matrix, as well as the lack of burnt clayey structures found in great amount e.g. in the 19th century low temperature natural cements (Weber et al, 2007) suggest that the raw material was virtually free of clay, i.e. no marlstone.

Carbonate grains with clear signs of high-temperature treatment exhibited by their margins and with remnants of quartz and feldspar embedded in them indicate the nature of the raw material used for calcinations. The most unusual appearance is exhibited by the aggregates with their corroded, cracked or zoned-altered surface. It is known that crystalline silicate phases such as e.g. quartz, feldspar or clay minerals do not have latent pozzolanic properties i.e. they do not react with $Ca(OH)_2$ in the presence of water in order to form hydraulic phases. However, most silicate aggregate fragments exhibit either a corroded surface filled with CSH phases, or some, mostly K-feldspar grains, exhibit a clearly zoned structure. Their outer Ca-rich rim is composed of Ca-silicates and aluminates, surrounded by with a dense, outer hydrate rim. Relicts of such phases always contain Ca in some percents, due to ion diffusion during the calcination process.

The presence of sparitic calcite and small amount of aragonite can be traced back to the thermal waters rich in dissolved calcium-carbonate. The different modifications of $CaCO_3$ are well-known and -analyzed in the vicinity of the bath and in the thermal caves of the Buda Hills.

The appearance of ettringite, found in all samples, is also known in historic hydraulic mortars. It may cause serious damages on the plasters due to the improper use of gypsum added to the lime to provide early strength of mortars. In the case of the mortars of the Rác Bath the sulphate source was not gypsum mixed to the paste as an accelerator for setting, but it originated from the thermal water of the spa rich in dissolved sulphate.

The analytical results clearly explain the excellent physical properties of the Ottoman mortars found in the Rác Bath. All samples show hydraulic nature that caused excellent hardness and durability of the material. The use of pozzolana as latent hydraulic additives in the white masonry mortars of this study can be excluded. With the exception of one brick fragment that was probably accidentally admixed to the paste neither artificial, nor natural additives with pozzolanic properties were identified in the samples.

We assume that the raw material of the mortars was a clay-free or clay poor limestone and/or limy sediment with relatively high amount of a well-sorted sand fraction composed mainly of quartz and feldspars. The Sarmathian oolithic, so-called coarse Sóskút Limestone would fit this criterion: its carbonate matrix contains variable amount of silicate grains. Although we have no information whether this stone could have been used for lime burning, it has to be noted that in the Ottoman baths of Budapest several Sóskút-stone blocks have been found, that were used for the construction of the buildings. The use of an “unknown” carbonatic sediment or sedimentary rock, such as e.g. a calcareous tuff or travertine rich in silicate sand fraction cannot be excluded either. There are several travertine occurrences known in the vicinity of warm water springs in Hungary containing large amount of quartz and feldspar grains cemented in their carbonate matrix.

During the calcination process silicate aggregates reacted with part of the carbonate and formed hydraulic phases. The uncommon appearance of the grains and the lack of typical outer margins of Ca-diffusion observed on silicate components of natural cements may refer to e.g. prolonged times of calcinations or inhomogeneous heat flow in the kiln. A smaller part of the lime that has not reacted with the silicates during the calcination can be found in the form of carbonate binder in the matrix.

We have no proof for the conscious use of such raw materials in order to obtain hydraulic mortars before the 18^{th} century. Yet it has to be emphasized that all samples were found either in the central arch or in the masonry of the building where sustainable structures has been constructed.

Reference

Weber, J., Kozlowski, R., Hughes, D., Gadermayr, N., Mucha, D., Jaglin, D.: Microstructure and mineral composition of Roman cement clinkers produced at defined calcination conditions, - Materials Characterization, Vol. 58, Issues 11-12, p. 1217-1228, 2007