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Investigation of medieval mortar and wall plaster from water reservoir by the fortified settlement at Mirkovo village, Bulgaria

Изследване на средновековен хоросан и мазилки от водохранилище в укрепено селище при с. Мирково, България

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Introduction

Cements is a term, describing various ancient stony bonding composite materials, used in building for consolidating and/or covering stone and brick or grains of sand. Some of these are cement, concrete, mortar, plaster, and stucco. The investigation of ancient cement composition shows the new knowledge for the surrounding environment and production technology. It may also elicit differences between the nature of original cement used for building and that used for later repairs. The methods of cements investigation include powder X-Ray diffraction for mineral composition determination and thermal analysis – for presence of calcite and/or aragonite, gypsum, clay minerals, origin of the gypsum – purposely added or products of late sulphation processes. Thermal analyzes also determinate the most important characteristic of cements – the hydraulic index by determining a water resistance index: the ratio of mass CO_2 losses at temperatures above 600 °C/mass losses of H_2O in the temperature range 200–600 °C (Goffer, 2007; Corti et al., 2013; Sáncheza et al., 2020).

The Medieval mortar and wall plaster from fortified settlement at Mirkovo village were studied by powder X-Ray diffraction and thermal analysis. The first and the only archaeological excavations of the fortified settlement (hillfort) at Mirkovo were conducted in 2012 after the project "Uncovering the upland zone archaeological heritage: a case study from the Mirkovo Basin, Bulgaria" with the cooperation between New Bulgarian University, Durham University and Northumbria University (Dumanov, 2012; Dumanov et al., 2012). The site is located in the south sections of Etropolska Planina on the peak Gradishte (1054.6 m). In his comprehensive study, Mutafchiev (1915) however missed the structures from the northwestern part of this region. Besides other archaeological complexes from the Mirkovo Basin Milchev (1961) was the first one who recorded the site in the late 50's of the past century. The hillfort is situated at the left shore of Rustaboaz valley. The valley is opened to the basin premising a nice approach towards the mountain ridges which have been the actual transport communications of regional and superregional importance. A Roman standing (burgus) was located at the entrance of the valley (Boyanov, 2011). The dale itself is closed from west by the hard ridge of Etropolska Baba peak reaching 1319 m altitude. The area of the plateau at the top is 9.5 da, as the size of the fortified zone is approximately the same. Remains of ramparts have been traced back on the three parts of plateau. The visible length of the wall is 212 m, as its width is varying between 0.70–1.80 m. The construction is of local shale blocks and implectum of crumb and pink or white sandy mortar. The buildings inside the enclosure are also built by shale blocks welded with wall plaster. The most solid building is located inside N-O8 squares i.e. at the highest point of the peak. Another important structure was partially disclosed by treasure-hunter's trenches as it has been defined as water reservoir. The reservoir is situated at the periphery of the site under the eastern slope of the site. The structure is dug into a layer dating to 10th century, as two periods of construction have been established. Presumably the cistern has been built in the middle of

11th century during the period of Byzantine restoration. The form is rectangular as initially the vat has been constructed by spalled stones and white mortar. Its total volume is 17 m^3. The inner side was covered by thick layer of hydrophobic mortar. At the second stage of construction (probably in 14th century), the inner part of the vat was strengthened with additional establishment built of stone, mortar and reused late antique tiles. This secondary addition was also covered with qualitative hydrophobic mortar. Pottery sherds and Ottoman silver coin from the middle of the 15th century mark the final stage in the existence of the fortified settlement. The end of the life in the hillfort probably was an aftermath of the first crusade of king Władysław III and János Hunyadi in 1443. The site is a nice example of the settlement patterns on the highlands surounding the western parts of the Sub-Balkan valleys.

The major issues studied in this paper are mineral composition determination and hydraulicity index calculations of mortar and wall plasters.

Materials and methods

A mortar from first building stage and wall plasters (1st and 2nd building stages) were collected from Medieval water reservoir of fortified settlement, situated at peak Gradishte, Mirkovo village (Mirkovo municipality, Sofia region) (Fig. 1a).

The powder X-ray diffraction (PXRD) measurements were made by Empyrean Powder X-ray diffractometer (Malvern Panalytical, Netherlands) in the 3–100° 2θ range using Cu radiation (λ = 1.5406 Å) and PIXcel3D detector. The database PDF (Powder Diffraction File, ICDD, 2001) was used for the determination of the phases and minerals present in the samples.

Thermal analyses (TG-DTG) were performed on a Setsys thermal analyzer (SETARAM, France) in air medium in the temperature range – from room temperature (RT) to 1050 °C, and heating rate of 10 °C.min^{-1}.

Results and discussion

Fig. 1b shows the samples PXRD patterns. The mineral composition of all samples was identified: quartz (SiO_2, #46-1045, 3.34Å), calcite ($CaCO_3$, #47-1743, 3.03Å), montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$, #07-0304, 4.48Å), hematite (Fe_2O_3, #33-0664, 2.70Å), anorthite ($CaAl_2Si_2O_8$), #41-1486, 3.18Å). The established minerals correspond to the mineral composition of local rocks – Triassic polymict carbonated sandstones and reddish clay limestones, and Precambian gneiss and amphibolite (Angelov et al., 1999). The mineral olivine ($(Mg,Fe)_2SiO_4$, #80-0943, 2.45Å) was detected as well. Its presence can be explained by the diabase bodies, located north of the region (Cheshitev et al., 1995). The ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$, #41-1451, 9.72Å) was recognized only for both wall plasters. This mineral typically formed at cement composites as wall plasters.

Fig. 1c and Table 1 present the results from Thermal analysis. The dehydratation of structurally bonded H_2O in the samples was defined by mass losses (ML) in the temperature range RT–600 °C. The samples from 1st building stage are with higher ML

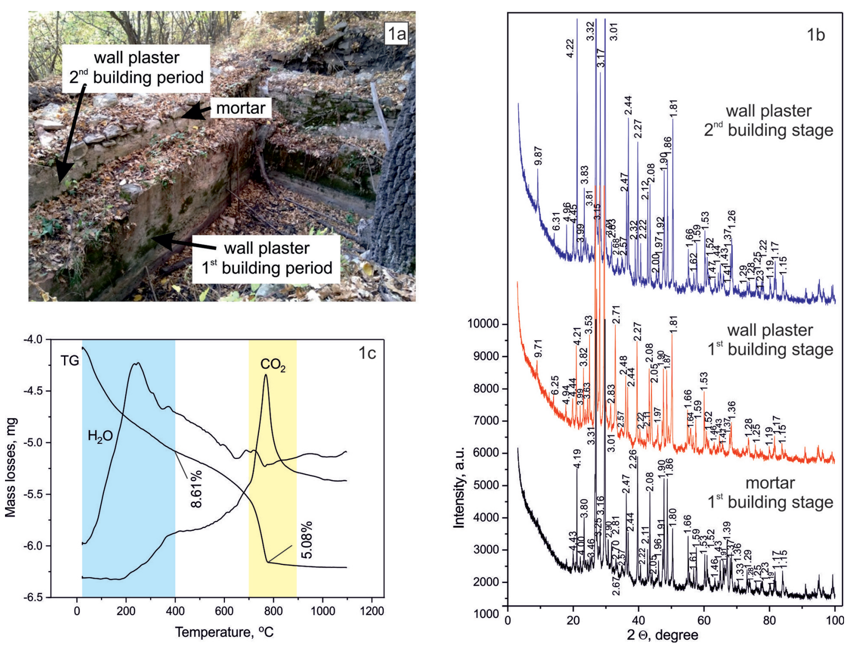

Fig. 1, *a,* water reservoir and place of sampling; *b,* PXRD patterns of studied samples; *c,* thermal analysis

Table 1. Thermal analysis – ML and calculated hydraulicity index

Sample	ML (structural H_2O) RT–600 °C, %	ML (CO_2) 600–900 °C, %	Hydraulicity index $ML(CO_2)/ML(H_2O)$
Wall plaster 2nd building stage	8.61	5.08	0.59
Mortar 1st building stage	11.91	7.72	0.65
Wall plaster 1st building stage	10.78	5.08	0.47

(10.78% and 11.91%) than that of 2nd building stage (8.61%), because of their close location to the earth surface and facilitated access to atmospheric water (Fig. 1a). The decarbonation of calcite was registered in temperature range 600–900 °C. The measured ML for the wall plasters from both building stages are equal (5.08%), which indicates an equivalent calcite amount. The higher ML for the mortar (7.72%) is due to higher raw calcite, as well as carbonation of calcium-silicate-hydrate (C-S-H) phase.

The mortar and wall plaster are composite, consisting of binder (usually clay), water, and filler (different aggregates such as sand, etc., giving strength after binder hardening). Depending on the type of hardening, the mortars and wall plasters may be divided into hydraulic and non-hydraulic. The hydraulic ones set and become adhesive due to a chemical reaction between the dry ingredients and water. The filler of studied samples was composed of quartz, anorthite and olivine, while the binder – of montmorillonite. The montmorillonite has negligible cementing ability, but finely grounded in the presence of water reacts with Ca-hydroxide ($Ca(OH)_2$) and forms cementitious compounds – calcium-silicate-hydrate(C-S-H) phases, to which it refers and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$). The montmorillonite binder suppose the type of studied composite to be a pozzolanic (Goffer, 2007; Corti et al., 2013; Sáncheza et al., 2020). This can be confirmed by hydraulicity index calculation. One way to calculate it is through ML – $ML(CO_2)/ML(H_2O)$ (Corti et al., 2013). There is a classification of hydraulicity index values and type of cement composite: hydraulisity index higher than 10 – “true” lime mortars; between 4 and 10 – hydraulic lime mortars; and <3 – pozzolanic mortars, i.e. lower $ML(CO_2)/ML(H_2O)$ ratios correspond to high hydraulic mortars (Corti et al., 2013). The hydraulicity index <3 has been calculated for the investigated samples (Table 1), and they can be referred as pozzolanic composites – waterproof and resistance to continuous contact with damp, conditions that were available in water reservoir.

Conclusion

The wall plasters and mortar from water reservoir are referred to hydraulic cements of pozzolan type. According to mineral composition, which corresponds to the mineral composition of the rocks in the area, it could be considered that most likely they were prepared by the local raw material. The investigated two wall plasters were made by the same material and technology of preparation in different building stages with an age difference of about 100 years. The ancient mortar was made by the same raw material, but with a larger amount of carbonate component, which probably increases the hydraulicity index up to 0.65 in comparison to 0.47 for the wall plaster from the same building stage.

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