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Original article

Laboratory-prepared lime-gypsum mixtures based on the know-how of traditional technology

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ABSTRACT

Stratigraphically, the oldest layer of paint which was applied to the facade walls of the Novo Celje Baroque Mansion contains substantial amounts of gypsum, as well as calcium carbonate and iron pigment. Microstructural, isotopic, and thermal analyses of facade samples were performed in order to exclude the possibility of an anthropogenic source of gypsum crystallisation, and to prove that natural gypsum was used to prepare the original lime-gypsum suspension. This is because, in the exothermic process of quicklime hydration, natural gypsum is converted into ß-hemihydrate and then, after cooling of the suspension, this compound is converted back into gypsum. The technology which was used for the laboratory-level preparation of the investigated lime-gypsum suspensions is simple, efficient, and sustainable, and could thus be used instead of the more energy-consuming dehydration processes which are presently used in the industrial production of gypsum.

1. Research aims

With regard to the technical issues which are involved in the renovation of historical materials, the presence of gypsum crystals is a phenomenon which is frequently attributed to the reaction between acid rain and the lime binder (i.e. secondary gypsum), and not to a primary building material (e.g. natural gypsum). The results of recent research into the properties of historical materials have shown that primary and secondary gypsum can be distinguished based on the identification of strontium, which is a characteristic of primary gypsum, but is not to be found in the secondary crystallisation products of gypsum. Strontium is an interesting marker which has already been used to prove the source of gypsum in historical materials [1], which is why it was also used in this research to confirm the source of gypsum as a natural resource for the preparation of lime-gypsum suspensions.

In modern industrial applications, thermal energy is used to dehydrate gypsum into β-hemihydrate. For this reason a hypothesis was established according to which, during the Baroque period, lime-gypsum suspensions were prepared by master builders in a manner which allowed them to take advantage of the exothermic reaction which takes place during lime slaking, and which also takes place if a mixture of quicklime and gypsum is slaked. It was taken into account that, during this period, the building material industry was not as highly developed as it is today, nor was thermal energy so easily accessible.

The technology which was used to prepare lime-gypsum suspensions was experimentally simulated in a similar manner to that used in the Baroque period, which can be concluded from the results of the investigations of one of the facade walls of the Novo Celje Baroque Mansion, the latter being one of the most typical such buildings belonging to this period in Slovenia.

2. Introduction

The Novo Celje Baroque Mansion is an impressive building which is located in the central part of Slovenia. It was built according to instructions given by Maria Theresa, the Austro-Hungarian Empress, for her Minister, Count Geisruck, between 1756 and 1764 [2]. After having been abandoned for more than two decades, conservation guidelines for the Mansion's renovation have been prepared by the Celje Regional Office of the Institute for the Protection of the Cultural Heritage of Slovenia (IPCHS), according to which, after the renovation works are completed, the facade walls will once again obtain their yellow-ochre Baroque appearance (Fig. 1).

For this purpose the layers of paint of one of the facade walls of the Novo Celje Baroque Mansion were analysed in detail. The

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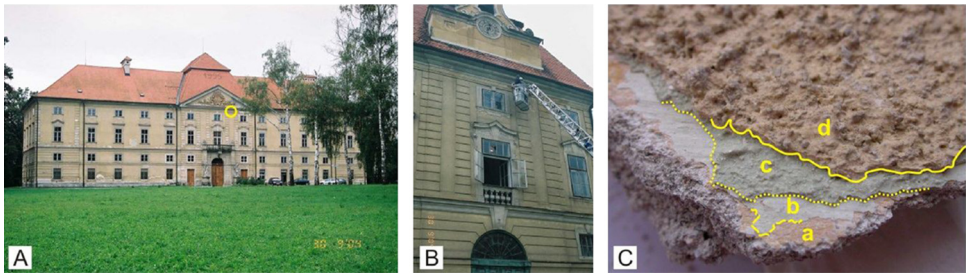

Fig. 1. A view of the north-facing facade wall of the Novo Celje Baroque Mansion, showing (A) one of the sampling locations, (B) the sampling work in progress, and (C) part of the sample from the facade wall.

results showed that, stratigraphically, the oldest layer of paint from the Baroque Era contained a large amount of gypsum, the source of which needed to be established; i.e. whether it was an anthropogenic source or whether natural gypsum had been added in order to prepare the lime-gypsum suspension. Gypsum (calcium sulphate dihydrate [$CaSO_4{\cdot}2H_2O$]) is a non-metallic mineral which has found a variety of uses in the construction industry. Over the temperature range between 120 °C and 170 °C the dehydration of gypsum takes place in a number of stages. Gypsum ($CaSO_4{\cdot}2H_2O$) is converted to a micro-crystalline form of β-hemihydrate ($CaSO_4{\cdot}1/2H_2O$), which is known in the construction industry as "plaster of Paris" or "stucco" [3]. The β-hemihydrate is ground and, upon the addition of water, used as a binder or for plasters [4,5]. Planned conservation and restoration works should, in the case of the given facade, rely on the results of this investigation, since gypsum from an anthropogenic source can harm the cohesion between materials, so that it has to be stabilised, by means of restoration interventions, into barium sulphate [6,7].

In humid climates, gypsum-based building materials are mostly applied in the interior of buildings due to the high solubility of sulphates in water, i.e. 2.1 g/L at a temperature of 20 °C [8], although the results of recent research into structures in North and Central Germany and in Italy have shown that gypsum-anhydrite mortars containing small amounts of lime have also been applied to the exterior of buildings [9]. Due to its low dehydration temperature, gypsum was used to prepare gypsum binders in Mesopotamia, as well as in Ancient Egypt, where it was used to help construct the pyramids. In Europe, it was mostly used in France (in the surroundings of Paris) and Germany (Bad Segeberg/Lüneburg, the Harz Mountains, and Franconia) [9,10], where large deposits of natural gypsum can be found. In Slovenia, there is only one gypsum site; it is located near the village of Dovje near the Slovenian-Austrian border, which is more of local significance considering its low availability [11,12]. Due to the limited availability in the past of gypsum as a natural resource for the needs of the construction industry, historical gypsum-based building products are extremely rare in the Slovenian architectural heritage, so that it was to be expected in only the most luxurious buildings in Slovenia, taking into account the reputation of the original owner of the Novo Celje Baroque Mansion.

3. Materials and methods

Stratigraphic research into the walls of the north- and south-facing facade walls of the Novo Celje Baroque Mansion included the taking of 21 samples of facade plaster with layers of paints that were first cast with binary epoxy resin in the laboratory. A sample of natural gypsum from Dovje was prepared in the laboratory in the same way, as well as a sample of the (new) laboratory-prepared lime-gypsum mixture. The surfaces of these samples were impregnated and then ground using abrasive paper of SiC granulation 800 and, finally, abrasive paper of granulation 4000, as well as being polished using 3 μm and 1/4 μm diamond paste. The mineralogical and chemical compositions of polished cross-sections of the samples were determined by Scanning Electron Microscopy (SEM), using JEOL 5500 LV SEM equipment with Energy Dispersive X-Ray spectrometry (EDS), in low vacuum mode (between 10 and 15 Pa), at an accelerating voltage of 20 kV and a working distance 20 mm. The X-ray spectra were optimized for quantification using the cobalt optimization standard, and correction of the EDS data was performed on basis of the standard ZAF-correction procedure, which is included in the INCA Energy software. This software was used to evaluate the results of the measurements, in order to confirm the natural source of the gypsum (through the presence or absence of Sr) in the Baroque-aged layer of paint taken from the north-facing facade wall of the Novo Celje Mansion, from the natural gypsum from Dovje, and from the new laboratory-prepared lime-gypsum material.

Raman spectra were obtained by using a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer coupled to an Olympus BXFM optical microscope. The measurements were performed using a 785 nm laser excitation line, a 100 × objective lens, and a 600 grooves/mm grating, which gave a spectral resolution of 1.99 cm^{-1}/pixel. A multi-channel air-cooled CCD detector was used, with integration times of between 20 and 35 seconds. The spectra are presented without any baseline correction.

In order to identify the age and, indirectly, the source of the gypsum used, and compare it to reference values [13] and [14], isotopic analyses of the sulphur isotope δ34S were performed on samples of the layers of paint which were taken from the Novo Celje Baroque Mansion, and on samples of natural gypsum from Dovje. These analyses were performed at the laboratory of the Helmoholtz Centre for Environmental Research, Germany, for Stable Isotopes–LSI, using the standard of precipitation of $BaSO_4$ + elemental analyser + IRMS and precipitation of ZnS + Kjeldahl + elemental analyser + IRMS.

Thermal analyses of the natural gypsum from Dovje, of the samples of paint taken from the facade wall of the Novo Celje Baroque Mansion, and of the lime-gypsum suspension developed in the laboratory, were conducted for comparison purposes. The tests were performed in the laboratories of Salonit Anhovo, on a STD 2960 analyser. The simultaneous digital thermal analysis and thermogravimetric (DTA-TGA) analyses were performed in an inert–N2 atmosphere with a temperature record interval of 10 °C/min, over the temperature range between 0 and 250 °C. In order to determine the maximum signal value, the observed correlation of derivations 1 and 2 of the TG signal was taken into account, along with reference data for phase transitions [15,16]. The characteristic temperatures were determined using the Universal Analysis for Windows 95/98/NT software, edition 2.5H.

4. Technology for the preparation of a new lime-gypsum suspension

The efficiency of the technology for the preparation of a new lime-gypsum suspension was proved indirectly through the

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