MINERALOGICAL AND GEOCHEMICAL STUDIES OF SECONDARY MINERAL ASSEMBLAGES RELATED TO DETERIORATION OF BUILDING MATERIALS

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Introduction

Crystallisation of secondary minerals, first of all salts, may substantially contribute to damaging of building materials. The most important damaging factor is crystallisation pressure during salt precipitation; producing stress in the substrate (Flatt et al., 2007). The chemical composition of secondary salts depends in general on natural and anthropogenic, internal and external factors (Manecki et al., 1997; Marszałek, 2016). They include particularly composition of substratum, climatic and topographic conditions, animal and microorganism activities, capillary rise of ground and soil waters, pollution of the atmosphere, as well as chemicals used for conservation processes.

Studies presented in this paper focused on the southern façade of the seventeenth century Myszkowskis Chapel of the Holy Trinity Basilica in Cracow, Poland. The façade is built of various materials: the characteristic rusticated wall is made of Tertiary Pińczów limestone blocks, covered with a cement render in its lower part. The exposed foundations are made of irregular fragments of bright, presumably Jurassic limestones, bound with and partly replaced by a cement and gray Carpathian sandstones. The wall reveals clear signs of damage ranging from dark gray soiling of the surface, scaling to efflorescences. The last ones occur mainly on the border between the limestone blocks and the cement replacements in a part of the foundations of the chapel.

Samples and methods

Samples for studies represent all type building materials used in elevation of the Myszkowskis Chapel and subwall with signs of deterioration and efflorescence. The building materials were analysed with optical microscopy, X-ray diffraction (XRPD) and mercury intrusion porosimetry mainly. Optical and scanning electron microscopy (SEM-EDS), X-ray diffraction (XPRD), and micro-Raman spectroscopy (RS) were used for identification of the secondary salts occurring in the deteriorated architectonical elements.

Results

Microscopic analysis revealed that all the materials analysed except cement mortars were covered with thin surface coatings. SEM-EDS analyses, particularly clearly in case of the Pińczów limestone samples, demonstrated that this outer zone was enriched in Ca, S and O, related to the presence of gypsum $CaSO_4 \cdot 2H_2O$. The shaft and bright blocks below are covered with several mm thick cement render. SEM-EDS analyses allowed to register presence of Ca, Si, Mg, Al, and O, sometimes Fe as well, apparently formed as a result of technological processes. XRPD analysis allowed to determine: calcite, portlandite $Ca(OH)_2$, ettringite $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$, quartz, dolomite, and monosulphite $Ca_4Al_2O_6SO_3 \cdot 11H_2O$. These components suggest presence of Roman or Portland cement.

Mercury porosimetry measurements indicated high porosity of the Pińczów limestones (24.66%, 31.54%) and relatively low of the subwall elements (15.30–18.33%). In most of the samples analysed pore size distribution patterns were bimodal, with domination of the pores in two ranges: 10.0–1.0 µm and 1.0–0.1 µm. However, the cement mortar sample displayed ca. 45% of the pores in the range 350–10 µm.

Most common secondary mineral is gypsum identified microscopically in some samples, and confirmed with XRPD analyses and micro-Raman spectroscopy. It occurs as platy crystals, up to several tens µm in length, sometimes in the form of cascades or rosettes. Halite NaCl forms irregular crusts and cubic crystals with distinct traces of dissolution. Its presence was determined only with the SEM-EDS analysis. Nitre KNO_3 and nitratine $NaNO_3$ were detected with SEM-EDS, on the limestone surfaces, close to the efflorescences. Nitratine was also found on the blocks of the rusticated wall. Anhedral crystals exhibited signs of dissolution. The presence of KNO_3 has also been inferred from its main Raman band at 1047 cm^{-1} and $NaNO_3$ based on its main band at 1064 cm^{-1}.

In the efflorescences the XRPD analyses allowed to identify sodium and potassium sulphates: thenardite Na_2SO_4, aphthitalite (glaserite) $(K,Na)_3Na(SO_4)_2$, and sulphate-nitrate salt – darapskite $Na_3(SO_4)(NO_3)\cdot H_2O$. Characteristic bipyramidal crystals of thenardite consisting of Na, S and O were up to 20 μm in length. Anhedral, often isometric crystals and irregular aggregates, in EDS analyses revealing the presence of Na, K, S and O, have been identified as aphthitalite. Euhedral, platy crystals of various length up to several tens μm, sometimes fan-shaped, consisting of Na, S, and O, have been identified as darapskite. The salts found in the efflorescences analysed suggest a complex system of solutions containing K_2SO_4–Na_2SO_4–$NaNO_3$–H_2O.

Conclusions

The salts dealt with in this study are hydrated and anhydrous compounds: simple salts – gypsum and thenardite/mirabilite, double salts – aphthitalite and darapskite. The anhydrous simple salts: halite, nitratine and nitre have been seldom observed. Other salts detected include ettringite and monosulphite. Gypsum, halite, nitratine, nitre and ettringite and monosulphite are present on the surface and/or inside the materials analysed, whereas thenardite, aphthitalite and darapskite form efflorescences on the border between the limestone blocks and the cement mortar in the part of the foundation. Formation of all the secondary salts recognised resulted in observed signs of deterioration of the Myszkowkis Chapel elevation.

Distribution of the salts clearly reflects the chemical composition of the substrate on which and/or within they crystallise. Occurrences of halite, nitre and nitratine in the limestone elevation of the chapel could be related to the high solubility and migration of these salts in the masonry. Thenardite, aphthitalite and darapskite, present only in the form of efflorescences are mostly related to the components of the cement mortars in replacements and joints.

The ions for precipitated salts could originate from both anthropogenic and natural sources. The most important external anthropogenic ones include: air pollution – wet and dry airborne deposition that provides mainly sulphate and nitrate anions, as well as road de-icing salts and detergent solutions used for cleaning for chloride ions. Other extrinsic sources of ions for precipitated salts could be also animal (e.g. excrements of birds) and microbiological activities.

Diversity of the secondary salt distribution (in form of crusts, efflorescences and/or inside the materials, in pores) should be linked to the differences in the structure of the pore spaces, susceptibility of the material to the crystallization of salts, and capillary condensation.

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References

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