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WALL PAINTING DAMAGE BY SALTS: CAUSES AND MECHANISMS

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ABSTRACT

Salts are one of the most dangerous degradation agents of artworks, especially in the environment of industrial pollution of 20th century. Salt damage in artwork causes not only mechanical changes by crystallization pressure, but also chemical and mineralogical alteration of its painted surface. That deterioration is especially serious on porous systems such as wall paintings. Salt removal by appropriate cleaning procedures is one of the principles of their restoration. For its optimal choice, it is crucial to know what salt is present and what is its source.

The main aim of the project was diagnosis of salt attack on wall paintings using non-destructive analysis of microsamples, identification of the attacking salts, and explanation of the alteration of Cu- and Pb-pigments. The work was performed in collaboration with artistic institutions. Results of laboratory experiments with porous materials, pigments, and salt solutions were compared with analyses of real artworks.

KEYWORDS: pigments, salt corrosion, X-ray microdiffraction,wall paintings

1. INTRODUCTION

The presence of salts is one of the main causes of deterioration of art objects with porous nature, particularly wall paintings and stone statues. Crystallizing salts may be locally concentrated as efflorescence on the artwork surface or as less apparent subflorescence in the subsurface of the porous materials that cause mechanical damages of artworks. Salts are hence considered one of the most dangerous degradation agents in cultural heritage and their removal by appropriate cleaning procedures is one of the principal goals of the restoration of artworks.

The course of salt corrosion of porous construction materials, such as stone, plasters, and concrete is relatively well explored in various research areas. Some authors (e.g. La Iglesia et al., 1997; Williams and Robinson, 1998) studied the crystallisation process of soluble salts inside the natural porous materials partially immersed in different saline solutions. Porous materials are suitable for migration of salt solution to the surface, where salt can crystallize and attack, for example, colour layers (e.g. Piqué et al., 1994). Studies of chemical degradation of pigments by their reaction with salts are much scarcer and less complete.

Because of pigments sensitivity to moisture, alkalinity and air pollution, some of them, such as azurite, orpiment, cinnabar, lead white and red lead, were not recommended for using in wall paintings (Šimůnková and Bayerová, 1999). Conversion to further salts can change the pigment colour, but even this fact cannot be easily revealed by examination of the artwork in its present state. One of the reasons is that it is not always possible to distinguish original phases and the products of their salt attack.

Many copper-based pigments are basic salts that are metastable if the activity of other ions changes during wetting the colour layer by salt solutions (e.g. Dei et al., 1998). However, many authors ignored these presumption because salts of copper are relatively cheap blue and green pigments.

Early Romanesque frescoes in the small church of St. George in Kostoľany pod Tríbečom, Slovakia, provide an example of the blackening of lead-based pigments. The wall paintings have been seriously damaged during the thousand years of their existence by both rain and ground water. After the last building reconstruction in 1960's, the wall paintings further faded because of their insufficient preservation and restoration, and unfavourable climatic conditions (Maříková-Kubková, 2006).

2. PROJECT OBJECTIVES

The main aim of this study is to describe the changes of selected pigments due to the action of different salt solutions and to try to understand the mechanism of the pigments alteration, to identify salts and determine them by using non-destructive methods of microsamples and to compare results from laboratory experiments with samples from real wall paintings.

3. METHODOLOGY

3.1. MATERIALS

In our experiments we used common burnt bricks (Kryry, Czech Republic), which were cut into three pieces of the same size (approximately 14 x 6 x 5 cm), and a sand from sand-pit Straškov (Tarmac CZ a.s., Czech Republic). The matured plaster was found in a building, which was built in the 17th century. The lime originated from restorer atelier and it was 7 years old. Some of the pigments used in the experiments were supplied by Kremer Pigmente, Germany: azurite (Azurit natur, 0-120 μ, product No. 10200), malachite (Malachit natur, 0-120 μ, product No. 10300), lead white (Flake White, product No. 46000), verdigris (Verdigris, product No. 44450). Some of the pigments were supplied as reagent grade chemicals: red lead (lead oxide, red, Lachema), massicot (lead (II) oxide, yellow, Lachema) and cerussite (lead carbonate, Penta). Basic copper carbonate was prepared according to a historical recipe.

Several fragment taken from the lead-containing dark brown part of the wall painting in Kostoľany and analysed by microdiffraction.

3.2. EXPERIMENTAL SETUP

Two types of experiments were carried out. In the first serie pigments reacted with salt solutions, in the second serie pigments were painted on the top of replicas of wall painting, which were submerged into salt solutions.

In the first type of experiments, pigments in the amount of 0.2g were suspended in Petri dishes with 5mL of salt solution (0.2M) and left to react up to one year. We used salts which are part of the environment (Na_2SO_4, $MgSO_2$, $CaSO_4$, NaCl, $NaNO_3$, $Ca(NO_3)_2$, Na_2CO_3, K_2CO_3 and urea), and additionally also salts applied on wall paintings during their cleaning and conservation ($NaHCO_3$, $KHCO_3$, $(NH_4)_2CO_3$, NH_4HCO_3). The reaction products were identified by X-ray powder diffraction (XRD).

Furher, we have carried out two types salt solution attack on replica of wall painting. Replicas of wall paintings were prepared as experimental bodies made of bricks covered by trilaminar plaster, prepared according to historical recipes from sand and lime. The pigments were painted with both "genuine fresco" (painting was applied on the wet plaster) and "secco" technique (painting was applied on the dried plaster).

Completed experimental bodies were placed into plastic boxes with salt solutions; boxes were closed with lids to avoid evaporation. The concentration of the salt solution was 0.2M. Salt solutions were let to soak into the experimental bodies to total depletion of solution. Then we sampled salt efflorescence from changed painting layers of the experimental bodies. We have used solutions of three salts ($NaHCO_3$, NH_4HCO_3, Na-EDTA) which are components of restorer cleaning agent Mora (AB 57), solution of NaCl and distilled water. We also prepared similar bodies from the matured plaster with thin layer of the fresh plaster to compare behaviour of the pigments in less alkaline environment.

Fragments were taken from several areas of the surface of the experimental bodies. In several cases we also scratched away the top layer of experimental body – a corroded pigment and salt efflorenscences. Powders were analysed by XRD with the same measurement conditions as were used for material analysis.

3.3. METHODS

All the solid material (bricks, sand, lime, pigments, reaction products, efflorescence, alterated pigments) was analysed by X-ray powder diffraction (XRD). X-ray patterns were collected with a PANalytical X'Pert PRO diffractometer with a detector X'Celerator in Bragg-Brentano geometry. Experimental set-up was following: CoK_α, 40 kV, 30 mA, line focus; angular range: 4-80°/2 Θ, step size: 0.0167°, counting time: 100 s.

To collect X-ray powder microdiffraction (μXRD) data from the top of fragments the same diffractometer was used. Experimental set-up was following: CoK_α, 40 kV, 30 mA, point focus, monocapillary (exit diameter of 0.1 mm), angular range: 4-80°/2 Θ, step size: 0.0167°, counting time: 2300 s.

Qualitative analysis was carried out with PANalytical X'Pert HighScore (version 1.0d) and PDF database (release 2004). An estimation of weight fractions of crystalline phases in all samples was carried out with the Rietveld method using the DiffracPlus Topas program (version 3.0, Bruker).

The samples of the used bricks and sand were treated following the Czech norm (CSN EN 772-5) for extraction of soluble salts from masonry to identify the major salts in them.

4. RESULTS

4.1. MATERIALS AND PURE PIGMENTS

According to XRD analysis the bricks are composed of quartz, feldspar, mica, and hematite, sand consist in quartz, mica, feldspars, and calcite. Composition of pigment is following: azurite (98 % azurite, 2 % malachite), malachite (99 % malachite, 1 % quartz), basic copper carbonate (43 % atacamite, 57 % paratacamite), verdigris (100 % hoganite), lead white (39 % hydrocerusite, 50 % amorphous phase and lead acetates, 6 % lanarkite, 5 % plumbonacrite), read lead (98 % minium, 2% massicot), massicot (89 % massicot, 5 % hydrocerussite, 6 % litharge) and cerussite (90 % cerussite, 10 % amorphous phase).

4.2. EXTRACTIONS

The extraction of soluble salts from samples of bricks showed that the extracted ions had the following concentrations: SO_4^{2-} (520 mg/kg), Cl^- (260 mg/kg), HCO_3^- (240 mg/kg), NO_3^- (10 mg/kg), Ca^{2+} (280 mg/kg), Na^+ (31 mg/kg), K^+ (25 mg/kg), Mg^{2+} (0 mg/kg). The ions extracted from sand had the following concentrations: HCO_3^- (460 mg/kg), SO_4^{2-} (32 mg/kg), Cl^- (19 mg/kg), NO_3^- (11 mg/kg), Ca^{2+} (150 mg/kg), Mg^{2+} (96 mg/kg), K^+ (28mg/kg), Na^+ (23 mg/kg).

4.3. EXPERIMENTS IN PETRI DISHES

Lead white reacts with salts to form the corresponding basic lead salt (e.g. with NaCl it forms laurionite PbOHCl**)** and then it slowly transforms to cerussite. These reactions are not accompanied by any colour change since the reaction products are white. The only exception is the reaction of lead white with sodium carbonates when stable greenish $NaPb_2(CO_3)_2OH$ is formed. Red lead (Pb_3O_4) has tendency to darken from orange to dark brown in all salt solutions containing dissolved atmospheric CO_2 due to disproportionation to plattnerite (PbO_2) and cerussite ($PbCO_3$). This reaction is promoted by light. Massicot (PbO) in wet state reacts with atmospheric CO_2 to form hydrocerussite and finally cerussite. Cerussite seems to be the most stable phase in the system.

All copper pigments darkened to tenorite with solution of Na_2CO_3 and K_2CO_3 due their high alkalinity. Malachite is the most stable pigment, it react only with NaCl to paratacamite. Azurite is less stable than malachite. Basic copper carbonate is reactive, it forms brochantite with sulphates and malachite with ammonium carbonates. Even more reactive is verdigris, which reacts in dependence on used salt and forms an appropriate secondary salt (e.g. brochantite, gerhardite, atacamite).

4.4. EXPERIMENTAL BODIES

Salt solutions penetrated to all bodies section during experiments. Salt crystallized on fresco surface and also on bricks free surface. If the Cu-pigments (azurite, malachite) were applied on wet plaster surface (“genuine fresco” technique), they darkened after several hours. XRD analysis showed that tenorite (CuO) is responsible for darkening of Cu-pigments. If the Cu-pigments were applied on dry plaster surface (“secco” technique), they did not darkened. Application of lead white by fresco technique was not accompanied by any colour change.

Lead white painted on surface of experimental bodies changed colour to greyish with light green, yellow and sometimes orange spots. In all experiments except Na-EDTA secondary phase of composion $NaPb_2(CO_3)_2OH$ was found by XRD in green and greyish spots. Analysis of yellow spot in experiment with NH_4HCO_3 showed presence of massicot (orthorhombic PbO). Analysis of orange spot in experiment with distilled water showed presence of litharge (tetragonal PbO). In the reaction with NaCl solution, a phase of composition $3PbO.PbCl_2.H_2O$ was formed.

Malachite and azurite darkened in most of the experiments after penetration of salt solution into the colour layer due to the formation of tenorite. This was probably due to high alkaline reaction of the penetrating salt solution in which $Ca(OH)_2$ from incompletely carbonated plaster was dissolved. No other copper containg secondary phase was found. Salt efflorescences consisted of sodium carbonates (trona $Na_3H(CO_3)_2.2H_2O$, thermonatrite $Na_2CO_3.H_2O$, natron $Na_2CO_3.10H_2O$) and burkeite ($Na_6(SO_4)_2CO_3$) when $NaHCO_3$ was used as a salt. Thenardite (Na_2SO_4) was formed in experimens with distilled water and $NaHCO_3$, although no sulphate anions were present in the used solutions. The sulphate anions originate probably from the bricks (see 4.2).

Efflorescence correspond to composition of used salt solution: SO_4^{2-} a Ca^{2+} created gypsum or burkeite $Na_4(SO_4)_{1.45}(CO_3)_{0.55}$; Ca^{2+} gaylussit $Na_2Ca(CO_3)_2(H_2O)_5$; Mg^{2+} boussingaultite $(NH_4)_2Mg(SO_4)_2.6H_2O$. Changed pigments content partly salt coming salt solution and partly the used pigments: chalconatronite $Na_2Cu(CO_3)_2(H_2O)_3$, $NaPb_2(CO_3)_2OH$, laurionite PbOHCl or gerhardtite $Cu_2(OH)_3NO_3$.

4.5. DARKENED PIGMENT IN WALL PAINTINGS FROM THE CHURCH OF ST. GEORGE IN KOSTOĽANY POD TRÍBEČOM

Samples taken from the darkened parts of the wall paintings were analyzed using µXRD to determine their phase compositions. Microdiffraction revealed the presence calcite, gypsum, and several different lead phases: hydrocerussite, cerussite, plattnerite (PbO_2), scrutinyite (PbO_2) and lead magnesium carbonate ($PbMg(CO_3)_2$).

To simulate the alteration process in the wall painting, we mixed red lead with an aqueous solution of Mg^{2+} and CO_3^{2-} ions. After 6 months of reaction a brown-red product was isolated that contained 51 % of unconsumed red lead, 26 % of $PbMg(CO_3)_2$, 13 %

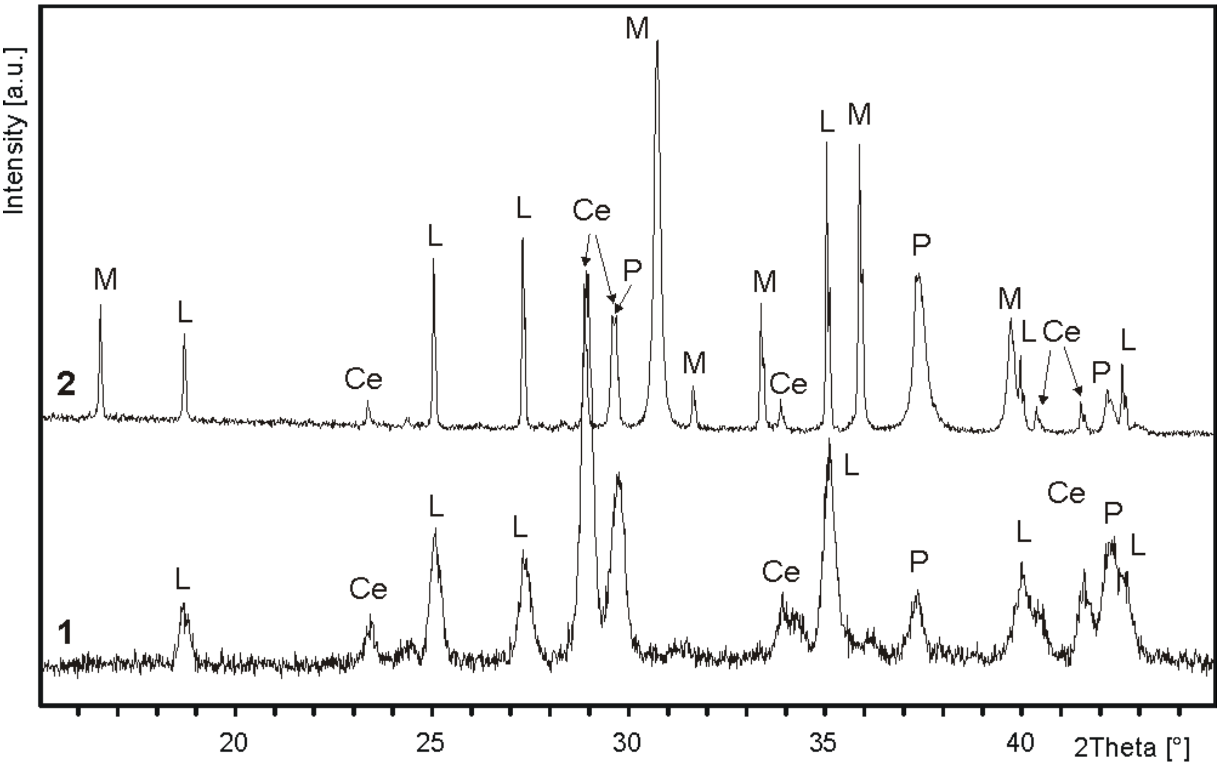

Fig. 1 Comparison of diffractograms. 1 - a fragment from Kostoľany wall painting, 2 - a reaction product of red lead with solution of Mg^{2+} and CO_3^{2-} ions after 6 months of reacting. Phase abbreviations: Mi – minium (Pb_3O_4), Ce - cerussite ($PbCO_3$), L - $PbMg(CO_3)_2$, P - plattnerite (PbO_2).

of plattnerite and 10 % of cerussite. The composition of our reaction product is in very good correlation with the composition of real microsamples from the wall painting (Fig. 1). The results of laboratory experiments suggested that the wall painting originally contained red lead that has since completely converted to PbO_2 and Pb(II) carbonates.

5. CONCLUSIONS

Lead-based pigments are not suitable for using in wall paintings since they degradate in the humid conditions to form lead carbonate (cerussite). Red lead darkens due to formation of plattnerite and cerusite. Copper-based pigments darken in alkaline environment and tenorite is formed. Malachite and azurite are more stable then basic copper carbonate and verdigris, which react easily with salt solutions.

The presence of cerussite or/and hydrocerussite (white pigments) in the paintings layer does necessarily indicate that lead white was used as an original pigment. These lead carbonates could have been formed by carbonatization of massicot or lead red.

Samples taken from a wall painting in the church of St. George in Kostoľany pod Tríbečom, Slovakia, were analyzed using X-ray powder microdiffraction to determine their phase compositions. Microdiffraction revealed the presence of several different lead phases: hydrocerussite, cerussite, plattnerite, lead magnesium carbonate. The results of laboratory experiments suggested that the wall painting originally contained red lead that has since completely converted to PbO_2 and Pb(II) carbonates

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PŘÍČINY A MECHANISMY POŠKOZENÍ NÁSTĚNNÝCH MALEB SOLEMI

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ABSTRAKT:

Soli patří k nejnebezpečnějším činitelům způsobující poškození uměleckých předmětů, zejména těch, které byly vystaveny vlivům průmyslového znečištění ve 20. století. Solná koroze uměleckých děl způsobuje nejen mechanické změny, jež jsou důsledkem působení krystalizačních tlaků, ale také chemické a mineralogické alterace barevné vrstvy. Solná koroze se projevuje zejména v porézních systémech, mezi které patří nástěnné malby. Odstraňování solí z jejich povrchu je základním úkolem restaurování. Pro správnou volbu restaurátorského postupu je přitom nezbytně nutné znát druh soli a její původ.

Hlavním cílem tohoto projektu byla diagnostika působení solí v nástěnné malbě s využitím nedestruktivní analýzy mikrovzorků, přesná identifikace solí a vysvětlení alterací pigmentů na bázi Cu a Pb. Projekt proběhl ve spolupráci s uměleckými institucemi. Výsledky laboratorních testů s různými porézními substráty, pigmenty a solnými roztoky byly srovnávány s analýzami vzorků z uměleckých děl.