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Original article

Analysis of calcium acetate efflorescences formed on ceramic tiles in a museum environment

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Abstract

Salt crystallization is a major cause of damage in porous materials such as stone, brick and ceramics. The paper reports results of an analytical study on tiles of glazed ceramics that are seriously damaged by acetate salt crystallization. Measurements of the ionic composition of the salt mixture in the tiles and in the efflorescences were carried out. Based on the available information on the phase equilibria in the system comprising of the main constituents chloride, nitrate, acetate, calcium and sodium, the crystallization pathways of the various solid phases are traced. It is shown that a combination of qualitative XRD analysis of the phases present in the efflorescences together with a quantitative determination of the ionic composition is sufficient for the quantitative analysis of major crystalline species in the efflorescences, i.e. $Ca_3(CH_3COO)_3Cl(NO_3)_2 \cdot 7H_2O$, thecotrichite, and NaCl, halite. The concentrations of these salts are obtained from a solution of the mass balance by least squares analysis. Their formation from the salt mixtures present in the tiles that are subject to acetic acid vapor attack is consistent with the solubility diagram of the above mentioned quinary system. Finally, the possibilities of preventive conservation of salt contaminated ceramics in typical museum environments are discussed.

Keywords: Salts; Ceramic tiles; Acetate efflorescence; Thecotrichite; Crystallization pathway; Preventive conservation

1. Introduction

Salt crystallization in porous building materials not only limits the durability of the world's architectural heritage but is also a major cause of damage in porous museum artifacts. Damage is caused by the growth of salt crystals in the porous structures of materials such as stone or ceramics. Acetate salts are frequently observed in efflorescences on calcareous objects in museum cabinets. Their formation is the result of the attack of acetic acid which is emitted by wood [1,2] and a number of other materials such as paints, resins or silicone-based sealants that are used for the construction of display cases [3]. The low air exchange rates in typical display cases and storage cabinets provide favorable conditions for the enrichment of volatile pollutants liberated by these materials. Grzywacz and Tennent [4] measured acetic acid concentrations in display and storage cabinets of several European museums and confirmed very high concentrations in wooden cabinets. They also observed high concentrations in very old cabinets (up to 120 years). Hence, acetic acid attack is not only the result of a high exposure in the past, but is an ongoing process leading to the continuous formation of acetate salts.

A number of different acetate salts were identified in efflorescences on museum objects. Pure calcium acetate was found on collections of egg-shells [5] and molluscs [6], a double salt, calcium acetate chloride pentahydrate, $Ca(CH_3COO)Cl \cdot 5H_2O$ [7], was found on both calcareous stone [8] and on ceramics [9]. An acetate nitrate double salt that was first identified on a coral brooch [10] was later characterized as dicalcium triacetate nitrate dihydrate, $Ca_2(CH_3COO)_3(NO_3) \cdot 2H_2O$ [11]. Finally, another widespread but initially unidentified

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efflorescence [12] was later characterized as the triple salt tricalcium triacetate chloride dinitrate heptahydrate, $Ca_3(CH_3COO)_3Cl(NO_3)_2 \cdot 7H_2O$, which was named thecotrichite [13,14].

Recently, the phase diagram of the quaternary thecotrichite system $Ca^{2+}{-}CH_3COO^-{-}Cl^-{-}NO_3^-{-}H_2O$ was established to understand the formation of the various double and triple salts mentioned before [15]. A total of nine different solid phases can exist in stable equilibrium with saturated solutions at 298 K. Both calcium chloride and calcium nitrate can exist in two different hydrated forms, hence, there are five different solids representing the pure salts, i.e. $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Ca(NO_3)_2 \cdot 3H_2O$, and $Ca(CH_3COO)_2 \cdot H_2O$. In addition, there are three double and a triple salt that can crystallize from mixed solutions, i.e. $Ca_2(CH_3COO)_3(NO_3) \cdot 2H_2O$, $CaCl(NO_3) \cdot 2H_2O$, $Ca(CH_3COO)Cl \cdot 5H_2O$ and $Ca_3(CH_3COO)_3Cl(NO_3)_2 \cdot 7H_2O$. Which of these solids is formed depends on the mixture composition and the ambient conditions, i.e. temperature and relative humidity. Hence, in order to assess the damage potential in a contaminated material it is important to know concentration and composition of the salt mixture present in the pore space and the environmental conditions as well. In the case of museum artifacts, the analysis of salts is usually problematic as the normal procedures of sampling and analysis cause unacceptable damage to the objects. In such cases, the analysis of wash solutions that are obtained during a desalination measure is an appropriate means for the determination of the soluble salt contents of an object.

In the present paper we report results of an analytical study on Dutch tiles of glazed ceramics that are seriously damaged by acetate salt crystallization. In previous papers [16,17] preliminary results were provided and discussed in the context of the conservation of the tiles and other ceramic objects from the same museum. Here, we focus on the analytical characterization of the salt system present in selected tiles and the formation of acetate containing phases. The ionic composition of the salt mixture in the tiles was deduced from the analysis of wash solutions. Direct sampling and analysis revealed the composition and nature of the efflorescences. It is shown that the quantitative speciation of the ionic constituents in the efflorescences is possible using least squares analysis. Based on the available information on the phase equilibria in the system comprising of the main constituents chloride, nitrate, acetate, calcium and sodium, the crystallization pathways of the various solid phases are traced. In particular, it is shown that the formation of thecotrichite efflorescences can be understood with the help of the phase diagram. Finally, the possibilities of preventive conservation of salt contaminated ceramics in typical museum environments are discussed.

2. Experimental section

2.1. Tiles and salt concentration reduction

In previous centuries glazed tiles, attached to damp walls of houses were often used to keep the humidity out. But as evaporation of the rising ground water did take place, through tiny cracks in the glaze, soluble salts, such as chlorides, nitrates and sulfates, accumulated in the tiles. In a previous study thecotrichite ($Ca_3(CH_3COO)_3Cl(NO_3)_2 \cdot 7H_2O$) was identified along with halite (NaCl), calcite ($CaCO_3$) and quartz (SiO_2) in efflorescences on lead-glazed ceramic tiles of the collection of the Stedelijke Musea in Kortrijk, Belgium in early 2001 [16]. At the end of 2001 further damage and efflorescences were noted on some 160 ceramic objects in the same museum. The present study is concerned with 72 tiles with biblical scenes executed in manganese on tin-glazed earthenware that are on display in a show-case on the same tile-panel. The tiles all measure $130 \times 130\ mm^2$ and are about 8 mm thick. The tiles of this group were badly damaged by salt crystallization as shown in Fig. 1. The unglazed backsides of most tiles were covered with a thick layer of fluffy needles of salt, in which tiny bits of earthenware were hidden. Some tiles had a badly pitted backside, some large cracks evolved and much debris was found on the bottom of the shelves. To conserve the tiles it was necessary to reduce the concentration of the salt by washing the tiles in different baths of demineralized water. Five tiles from this group were selected to determine the salt content in the efflorescences and in the wash solutions.

2.2. Sampling

Efflorescences were collected by careful brushing and weighed. Sample sizes varied from 120 mg to 274 mg. Known weights of the efflorescences were dissolved in doubly distilled water and the solutions were filtered to remove insoluble particles consisting mainly of grains of ceramic material lifted off during the growth of the efflorescences.

After removal of the efflorescences, the tiles were washed in a bath of 2 L of demineralized water. The tiles remained in the bath for several days and the procedure was repeated six times. The efficiency of the salt concentration reduction was monitored by measurements of the conductivity of the wash solutions at regular intervals. To accelerate the diffusion process, the water was changed every 24 h during the first two days (bath 1 and bath 2, respectively). Subsequently, the water bath was changed if the increase in conductivity indicated a significant slow-down of the salt mobilization. The extraction times for baths 3, 4, 5 and 6 were 9, 25, 12 and 21 days respectively. About 20 mL of all wash solutions were stored in a refrigerator in HDPE bottles until they were used for the final measurement of the conductivity at constant temperature and the determination of the ion concentrations.

2.3. Instrumentation

Conductivity in the baths was measured by a multi-parameter instrument and conductivity cell (pH/Cond 340i and TetraCon 325, WTW, Weilheim, Germany). All conductivities were measured at 19 °C. XRD parameters were obtained on a Bragg–Brentano parafocusing reflection diffractometer