

THECOTRICHITE ON SALT CONTAMINATED CERAMICS

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INTRODUCTION

Formation of acetate salt efflorescences on calcareous artefacts is a widespread problem in museum cabinets containing wood products. In the Broelmuseum in Kortrijk (Belgium) damage caused by efflorescences has been observed on over 200 objects since 2000. Five tiles were selected to determine the salt content by ion chromatography (IC), atomic emission spectroscopy (AES) and X-ray diffraction (XRD).



Fig. 1 Dutch tin glazed tiles (18th century) in display case: efflorescences and damage.

TILES

Serious damage caused by salt crystallisation can be observed in fig. 1. The unglazed sides were covered with bundles of long whiskers, debris of ceramic material was found underneath the tiles and large cracks evolved. Efflorescences were collected by careful brushing. Thecotrichite $\text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$, halite, calcite and quartz were found by XRD analysis. The brushed tiles were each washed in six different baths of demineralised water. Sodium, calcium, acetate, chloride, nitrate and sulfate concentrations were measured in the wash solutions and the efflorescences to determine the total amount of soluble salts. The tiles contained high concentrations of soluble salts, whereas significant amounts of acetate were only found in the efflorescences. In contrast, most of the chloride and nitrate was found in the wash solutions, hence, in the tiles rather than in the efflorescences (see table 1).

Tab. 1 Soluble salts and molar ratio in the tiles

Tile No.	Total soluble salts in tiles (g)		Acetate in efflorescences (g)	Molar ratio Cl ⁻ / NO ₃ ⁻
	tiles (g)	efflorescences (g)		
1	5.58	0.0530	0.0169	0.98
2	5.80	0.0457	0.0150	1.18
3	6.29	0.0422	0.0129	0.99
4	6.96	0.1049	0.0364	0.96
5	7.11	0.1269	0.0444	1.05

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PHASE DIAGRAM

Solubility measurements of the $\text{Ca}(\text{CH}_3\text{COO})_2\text{-CaCl}_2\text{-Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ system were carried out and several different solids were identified by X-ray diffraction and ion analysis. The phase diagram of the system, depicted in fig. 2, was calculated using an equilibrium model. All possible solution compositions can be expressed as the molar ratio of $\text{Ca}(\text{CH}_3\text{COO})_2$, CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ in a triangular diagram. The corners represent the pure salts, the lines in the interior give the compositions of saturated solutions coexisting with two solid phases. The invariant points (blue points) reflect the compositions of solutions coexisting with three solid phases. The stability fields (1 to 10) between the lines represent compositions of solutions saturated with respect to only one solid phase. The composition of the salt minerals is indicated by the red symbols.

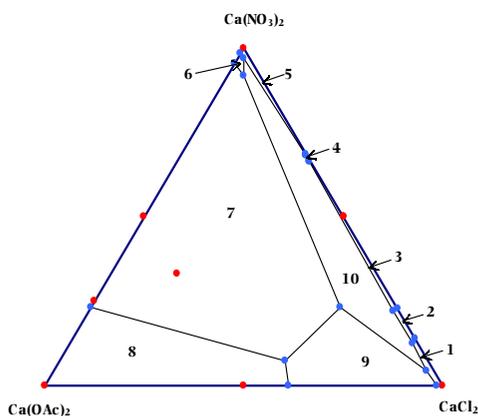


Fig. 2 Solubilities in the $\text{Ca}(\text{CH}_3\text{COO})_2\text{-CaCl}_2\text{-Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ system at 25°C, solid phases corresponding to the stability fields are: (1) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, (2) $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, (3) $\text{CaCl}(\text{NO}_3) \cdot 2\text{H}_2\text{O}$, (4) $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (5) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, (6) $\text{Ca}(\text{CH}_3\text{COO})(\text{NO}_3) \cdot 3\text{H}_2\text{O}$, (7) $\text{Ca}_2(\text{CH}_3\text{COO})_3(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, (8) $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, (9) $\text{Ca}_2(\text{CH}_3\text{COO})\text{Cl} \cdot 5\text{H}_2\text{O}$, (10) $\text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$

DISCUSSION

The molar ratios of chloride and nitrate (last column of table 1) represent the composition of the salt mixtures that were originally present in the tiles before they were exposed to an acetic acid environment. Such mixtures are extremely hygroscopic and the crystallisation of the double salt $\text{CaClNO}_3 \cdot 2\text{H}_2\text{O}$ (phase 3 in fig. 2) would occur only at relative humidities below 20%. Most likely the salt mixture remains in solution at all times. However, as the acetate concentration increases as a result of acetic acid deposition, the composition of the solution moves into the stability field of thecotrichite (phase 10 in fig. 2). Due to its much lower solubility thecotrichite precipitates in the pore space close to the surface where the crystal growth causes stress. Hence, only a relatively small amount of acetate formation is responsible for the observed damage.

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