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Study of nitrate contaminated samples from a historic building with the hygroscopic moisture content method: Contribution of laboratory data to interpret results practical significance

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ABSTRACT

The assessment of moisture and soluble salt sources affecting the masonry materials of a historic building located in the Old Town of Prague triggered the present experimental research focused on the use of the hygroscopic moisture content (HMC) method for the evaluation of nitrate salts in building materials. The historic building under study had been recently subjected to a rehabilitation intervention that encompassed the injection of a damp-proofing chemical at the ground level and the application of renovation mortar coats. The applied renovation plasters and renders showed striking moist stains within 6 months after their application. To unveil the reason behind the moist-related problems observed, several samples of repair plasters and renders, as well as of the underlying historic masonry materials, were collected from representative affected areas of the building. The HMC method combined with ion chromatography (IC) was used to investigate the nature and amount of soluble salts in the specimens. Nitrates were generally found in a high content and located at high levels (ca. 3 m height) in the walls. The IC results and the generalised surface wetting observed on-site led us to infer that nitrocalcite was one of the main salts present. The results obtained instigated a laboratory study with the HMC method to assess the hygroscopic behaviour of single nitrate salts and salt mixtures. The selection of single salts and the design of the salt mixtures was based on the IC data of the selected historical materials' samples aiming at replicating their hygroscopic behaviour. The results of the case study indicated that the rehabilitation strategy implemented reduced the rising damp phenomena, but that the choice of the type of mortar coats may have contributed to drawing existing moisture (and salts) to higher levels in the walls. The evaluation of the hygroscopic behaviour of samples with the HMC method at a range of RH provided a better understanding of the on-site behaviour of the salt-contaminated materials in the building. The results of the laboratory study showed that the salt mixtures prepared simulated well the hygroscopic behaviour of the building samples.

1. Research aims

The hygroscopic moisture content (HMC) method is a simple laboratory technique that can be used to assess the sources of moisture and soluble salts in building materials. The HMC method has already been the focus of a few laboratory research studies for assessing the hygroscopic behaviour of common salts found in buildings [1–3]. In this study, the experimental research focused on the hygroscopic behaviour of the most common nitrate salts found in a historic building located in the Old Town of Prague. The composition and distribution of the salts and associated moisture problems were the basis for devising the experimental laboratory programme in this work. The research aims were the following:

- to assess the moisture and salt sources in a historic building using the HMC method;
- to characterize the hygroscopic behaviour of salt-contaminated building samples collected on-site in a range of relative humidity levels;
- to distinguish different single nitrate salts based on their hygroscopic behaviour;
- to compare the hygroscopic behaviour between single nitrate salts and their combination;

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- to replicate the salt composition of the samples collected on-site based on their ionic composition and verify their hygroscopic behaviour.

2. Introduction

Salt weathering is considered one of the most severe damaging mechanisms of building materials in a broad range of environmental conditions [4]. Soluble salts originate from ions originally present in building materials and from external sources (e.g. atmospheric aerosols, ground pollutants absorbed by capillary action, biocolonization). Salt weathering and chemical weathering are considered different degradation mechanisms, but they operate together; the salts resulting from chemical dissolution reactions are usually more soluble than the parent compounds, which are subsequently involved in dissolution-crystallization cycles [5]. The presence of soluble salts in building materials, their type, quantity, source and distribution, are important parameters to take into account before carrying out a repair treatment. Their assessment is typically based on the quantification of common ions (Ca^{2+}, Mg^{2+} Na^{+}, K^{+}, $SO_4{}^{2-}$, $NO_3{}^{-}$, Cl^{-}, $CO_3{}^{2-}$) present in the soluble extract of samples of deteriorated materials, desalination poultices and/or of salt efflorescences. However, the low cost of the type of analysis commonly used to identify and quantify soluble salts is often a reason for limiting the extent of the survey. In addition, the behaviour of different mixtures of salts in a material (e.g. solubility, mobilisation, deliquescence point) is difficult to predict based solely on their composition. The prediction of the hygroscopic behaviour of soluble salts is important for planning a conservation intervention. The ECOS-RUNSALT program [6,7] has become a popular tool to predict the range of deliquescence RH of complex salt mixtures. Nevertheless, experimental investigations are important for validation of the model predictions and for illustration of kinetic effects [8].

Recent studies [2,3,9–11] have focused on the potential of the hygroscopic moisture content (HMC) as an alternative and/or complementary method to chemical analysis for evaluating the moisture and salt sources in building materials. The method consists of extracting samples by e.g. drilling the material while collecting the powder and, after drying, subjecting the samples to a determined relative humidity (RH) level until reaching a constant weight. Water soluble salts have a characteristic hygroscopic behaviour and adsorb moisture from the air above their equilibrium RH (RH_{eq}). If there are salts present in the samples, an increase of weight is registered, which depends on the type and amount of salt. In this way, the HMC values can be used to examine whether a source of moisture exists or if the actual moisture in the samples is solely assigned to the hygroscopicity of the salts present. Diaz Gonçalves and Delgado Rodrigues [9] explained the fundamentals and accuracy of the HMC method. The same team [1] performed tests on pure salts (NaCl, KCl, $NaNO_3$, KNO_3, K_2SO_4, K_2CO_3, Na_2SO_4, Na_2CO_3, $CaSO_4.2H_2O$) and showed that there is a very clear proportionality between the salt content and their HMC. The tested materials (lime mortar and brick) had no significant influence on the results, indicating that the HMC was governed by the hygroscopic behaviour of the salts present. Moreover, no relevant differences were found between the results obtained for three cohesion states of lime mortar samples (powder, granular, and entire pieces) [1,2]. Another study [12] demonstrated that the deliquescence of calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) can be influenced by the type of support on which the salt is deposited; in some cases, the support worked as a catalyst in increasing the rate of water sorption.

For a pure salt, it is relatively simple to determine its amount in a material, as long as the relation between the salt content and its hygroscopic behaviour is known. However, different salts are usually present on-site and the analysis of their hygroscopic behaviour can be very complex. The HMC is usually determined at 95–98% RH [1,3,9,10,13] because it is virtually above all the deliquescence and RH_{eq} of the most common salts present in building materials.

The main goal of this work was to assess the moisture and salt sources in a historic building and to study the behaviour of different single salts and salt mixtures using the HMC method. The paper is organised into six sections. The following section gives the theoretical outline of the HMC method. Section 4 gives a description of the historic building and of the rehabilitation intervention performed, details the methodology adopted to assess the moisture-related problems found, and presents and discusses the results obtained. The Section 5 describes the experimental laboratory programme devised to study the hygroscopic behaviour of the typical nitrate salts found in the historic building and the results are given and discussed. Finally, the main conclusions are drawn in Section 6.

3. Theoretical approach

Soluble salts can dissolve in liquid water by adsorbing moisture from the ambient air when the RH is higher than the water activity of a saturated solution of the particular salt or salt mix. The water activity is characteristic for each salt (or salt mix) and may also depend on temperature. If the RH drops below the water activity of the saturated solution, water evaporates and the salt precipitates [14]. A salt solution can become increasingly diluted with rising RH. The molality of a solution (moles of salt/litre of water) can be calculated by the following equation, which gives a functional relationship between the molality of a solution and the RH of the air [15]:

$$\ln\varphi = \ln a_w = -n\phi{\cdot}M_w{\cdot}m \tag{1}$$

where: φ is the RH (%); a_w is the water activity of the solution (%); n is the no. of ions in the salt; ϕ is the osmotic coefficient; M_w is the mole weight of water (kg/mol); and m is the molality of the solution. The osmotic coefficient is dependent on the molality and temperature of the electrolyte solution and must be found empirically. With Eq. [1], a linear curve can be derived from the salt amount and its equilibrium hygroscopic moisture content in an environment at constant RH. As described by Diaz Gonçalves and Delgado Rodrigues [9], another technique that can be used for correlating the HMC of the sample with the value of its salt content is by performing directly a series of HMC measurements on laboratory samples contaminated with known amounts of the salt. If the thermodynamic properties of the salt are not known and it is difficult to replicate its composition in the laboratory, the HMC method may still be used on a quantitative basis, but only for carrying out a relative quantification (comparison of the salt content in different samples) assuming that the type of salt is relatively similar in all samples [9]. The complexity of the analysis is higher for a solution with a mixture of three or more ions because the solubility of each salt depends on the concentration of the various ions present. The thermodynamic properties of mixed electrolyte solutions can be analysed with the Pitzer ion interaction model [16]. This model has been used by several authors to study binary and ternary aqueous electrolyte solutions, e.g. [5,17,18]. In this paper, the research was focused on comparing the hygroscopic behaviour between single nitrate salts and their combination.

4. Case study

4.1. Description

This work is centred in a complex of mediaeval buildings in Prague's Old Town that was subject to a recent rehabilitation inter-