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The role of marine aerosol in the formation of (double) sulfate/nitrate salts in plasters

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ABSTRACT

During decades the use of gypsum in different buildings has been very common, especially in the Atlantic lands of Europe. Decay compounds like salt crystallizations are ones of the principal deterioration factors of such historical buildings. In this study, gypsum-based plasters from different inner rooms of the Igueldo Lighthouse (San Sebastian, Spain), a building dated back to 1860 that has been subjected to several repairs within these years, were investigated in order to ascertain the main mineral phases produced during the weathering process. A combination of Raman spectroscopy, X-ray diffraction, infrared spectroscopy in ATR mode, SEM-EDS imaging and Raman imaging was successfully applied to study the distribution of different decay compounds in the gypsum-based matrix and to establish the decay reaction pathway which leads to the formation of the identified decay compounds. Additionally thermodynamic chemical modeling was also performed to explain the formation of specific decaying compounds. According to the location of Igueldo Lighthouse (just above a cliff, close to the sea), this building experiments a wide influence of the marine aerosol (Na^+, K^+, Mg^{2+}, Cl^- and NO_3^- input) and the influence of a high damp environment, giving rise to common efflorescence salts as well as to different mixed-calcium sulfates and mixed sulfate–nitrate salts, such as glauberite, syngenite, polyhalite and humberstonite. Dehydration process of gypsum from the plaster (leading to the presence of anhydrite and bassanite) was also identified.

1. Introduction

Gypsum ($CaSO_4 \cdot 2H_2O$) is one of the oldest materials used in construction. In the Neolithic period, with the development of fire based technologies, calcined gypsum plaster began to be developed, and it was used to assemble the pieces of masonry, seal the joints of the walls and to cover the walls of the houses, being progressively an alternative to the mud mortar. Since that time it began using regularly until nowadays, especially in the Atlantic lands of Europe. During production process, depending on the temperature and duration of the heating, gypsum converts to the hemihydrate (bassanite $CaSO_4 \cdot ½H_2O$) or to an anhydrous form (anhydrite $CaSO_4$). Water partial pressure control is difficult and thus $CaSO_4$–H_2O system highly variable and phase equilibrium depends on grain size and thermal treatment kinetics. Recent studies have demonstrated that, under atmospheric pressure [1,2], there are up to five compounds produced in this system, such as $CaSO_4 \cdot 2H_2O$ (gypsum, monoclinic), $CaSO_4 {\cdot} ½H_2O$ (bassanite monoclinic/rhombohedral), γ-$CaSO_4$ (anhydrite I, or AI, cubic), β-$CaSO_4$ (anhydrite II, or AII, orthorhombic) and α-$CaSO_4$ (anhydrite III, or AIII, hexagonal). Depending on the pressure (neon gas as pressure-transmitting medium) and gradient, different mineral phases in the dehydration of the $CaSO_4$–H_2O system can suffer deformations in their structure [3,4].

In the literature there are several studies that remark also the high influence of organic and inorganic additives which they have been used since the second half of the 20th century in order to control the hydration in gypsum setting/production [5–7]. Sometimes NaCl, $MgCl_2$, $CaCl_2$ solutions can dehydrate gypsum as a result of the lower water vapour pressure of these solutions, modifying its solubility [8]. The later compounds, together with nitrates and sulfates, are present in marine aerosol [9], besides of fatty acids [10]. Some authors point out that in marine aerosol a mixture of ions like Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, Br^-, I^-, Li^+, NO_3^- , NH_4^+, SO_4^{2-} and CO_3^{2-} are usually present along with structural water and other less common ions from anthropogenic sources (e.g., Ba^{2+}, Sr^{2+}, Pb^{2+}, VO_2^-) [11–13]. In this way, in the marine aerosol composition, natural and anthropogenic ion inputs are present [14,15]. There are studies that simulated the reactions between cations and anions in the complex Na^+, K^+, Ca^{2+}, Cl^-, SO_4^2 — –H_2O system [16],

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which can occur in natural environment, promoting the formation of different type of sulfates.

In the literature, several studies describe the formation of decay compounds in building materials as a consequence of the reactions between the original compounds and the ions transported in the marine aerosol. The main pathologies promoted due to these reactions are the formation of efflorescence, sub-efflorescence, loosing and detachment of the building materials, etc. [17–22]. Different decay compounds which have been detected inside the porous and/or over the gypsum surface or in presence of gypsum are listed in Table 1.

Moreover, theoretical models based on density functional theory calculations of the structures and properties of compounds like anhydrite ($CaSO_4$), polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$) and carnallite ($KMgCl_3 \cdot 6H_2O$) (the last two related with marine influence) have been studied [33]. Other authors, using techniques such as XRD and SEM-EDS have demonstrated the influence and direct relationship that exists in the formation of gypsum and glauberite with the marine aerosol; and their seasons' dependence/periodicity [34].

In this work, a combination of different analytical techniques, including Raman spectroscopy, X-ray diffraction and infrared spectroscopy in ATR mode have been used to identify different decay compounds formed on gypsum plasters from indoor areas of an historical building located in front of the sea, the Igueldo Lighthouse (Donostia-San Sebastian, north of Spain). Moreover, to complete and corroborate the point-by-point spectroscopic results, SEM-EDS imaging and Raman imaging were used to map the distribution of the different decay compounds crystallized on gypsum-based plasters. Finally, thermodynamic calculations to complete the analytical statements taking into account the high influence of marine environment were carried out.

2. Materials and methods

2.1. Samplings

Plaster samples from the walls of the Lighthouse machine room, where the temperature conditions inside the room range between 27 °C (winter time) and 35 °C (summer time) with a wide range of relative humidity (>90%) were collected using a scalpel. The size of all of them never exceeded 2×2 cm^2. Plaster fragments were analyzed directly by means of point-by-point Raman spectroscopy. For the XRD, ATR-FTIR, SEM-EDS imaging and Raman imaging, the same samples were powdered.

2.2. Instrumentation

The SEM-EDS analyses were carried out using a EVO®40 Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) coupled to an X-Max energy-dispersive X-ray spectrometer (Oxford Instruments, Abingdon, Oxfordshire, United Kingdom) for electron image acquisitions and elemental analysis (punctual and imaging). Although gypsum alone is not conductive, it was possible to obtain optimal results without carbon or gold coating. The SEM images were obtained at high vacuum employing an acceleration voltage of 30 kV and a 10–400 μm working distance. Different magnifications (reaching up to × 6800) were used for secondary electron images and an integration time of 50 s was employed to improve the signal-to-noise ratio. The EDS spectra were acquired and treated using the INCA software. Furthermore, a mapping of specific microscopic areas in the samples was possible, allowing the evaluation of the distribution of these elements over the sample.

Table 1
Mineral phases identified in plaster.

Mineral phase	Chemical formula	Reference
Bassanite	$CaSO_4{\cdot}½H_2O$	[21]
Anhydrite, types I, II and III	$CaSO_4$	[1,23]
Glauberite	$CaNa_2(SO_4)_2$	[24,25]
Thenardite	Na_2SO_4	[26,27]
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	[28]
Metastable mirabillite	$Na_2SO_4 \cdot 7H_2O$	
Mascagnite	$(NH_4)_2SO_4$	[21]
Epsomite	$MgSO_4 \cdot 7H_2O$	[29]
(para) Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$	[27]
Syngenite	$K_2Ca(SO_4) \cdot H_2O$	[29]
Starkeyite	$MgSO_4 \cdot 4H_2O$	[21]
Hexahydrite	$MgSO_4 \cdot 6H_2O$	[30]
Eugsterite	$Na_4Ca(SO_4)_3 \cdot H_2O$	[30]
Darapskite	$Na_3(SO_4)(NO_3) \cdot H_2O$	[31]
Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$	[32]

ATR-FTIR spectra were recorded using a Bruker Equinox 55 spectrometer equipped with an extended KBr Beamsplitter and purged with dried air. A liquid nitrogen-cooled MCT detector or a Peltier-cooled DTGS Mid-IR detector was used. Two hundred scans were accumulated between 4000 and 600 cm^{-1} with a 4 cm^{-1} resolution with the help of an extended KBr Beamsplitter. A background was collected before each sample's spectra and additional atmospheric compensation was provided by Opus 6.5 Software. Few milligrams of sample powder are required for each measurement using an ATR diamond crystal accessory (Golden Gate®, Specac) which no require any additional sample preparation constraints. The obtained spectra were compared with the spectra of pure standard compounds contained in RRUFF [35] and in the e-VISART infrared databases [36].

The XRD analyses were performed with a PANalytical Xpert PRO powder diffractometer, equipped with a copper tube ($\lambda_{CuK\alpha1} =$ 1.54060 Å, $\lambda_{CuK\alpha2} = 1.54439$ Å), vertical goniometer (Bragg–Brentano geometry), programmable divergence aperture, automatic interchange of samples and secondary monochromator from graphite and PixCel detector. The measurement conditions were 40 kV and 40 mA, with an angular range (2θ) scanned from 5 to 70°. The X'pert HighScore (PANalytical) software in combination with the specific powder diffraction file database (International Centre for Diffraction Data-ICDD, Pennsylvania, USA) was used for the phase identification.

For micro-Raman spectra and Raman Imaging, a Senterra spectrometer (Bruker Optics, Karlsruhe, Germany) equipped with a Peltier-cooled charge-coupled device detector and × 10 and × 50 long working distance Olympus objectives was used to collect the Raman spectra excited under a 785 nm light from a diode laser. The Raman image acquisitions of specific areas of the plaster matrix were conducted using the Peak Pick Singular option. The interpretation of all the Raman results was performed by comparing the acquired Raman spectra with the Raman spectra of pure standard compounds collected in the e-VISNICH dispersive Raman database [37]. Additionally, free Raman databases (e.g. RRUFF [35]) were also considered for the assignation of unknown Raman bands. Different spectral analysis tools, OPUS© 7.0 (Bruker Optik GmbH, Ettlingen, Germany (2011)) for Raman Imaging; and Omnic 7.2 (Nicolet) and Wire 2.0 (Renishaw) for spectral treatment and assignation, were used.

Thermodynamic chemical modeling was also performed to explain the formation of specific decaying compounds, considering the composition of the plaster and the input of ions infiltrated in the material. For that purpose the MEDUSA [38] free academic program was used. This program implements its own Hydrochemical Equilibrium-Constant (HYDRA) database. This database was extended manually introducing the logarithm of the formation constant of specific mineralogical phases of interest [39]. Certain constants were obtained also from the Visual MINTEQ [40] database.

3. Results and discussion

3.1. Point-by-point Raman spectroscopy analyses

In the Raman spectra acquired on the gypsum plaster samples, different kind of sulfates and nitrates bands were distinguished. Most of the bands are centered between 960–1080 cm^{-1} as in Fig. 1 is illustrated.