Construction and Building Materials 170 (2018) 290–301

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Conversion of calcium sulfate dihydrate into calcium phosphates as a route for conservation of gypsum stuccoes and sulfated marble

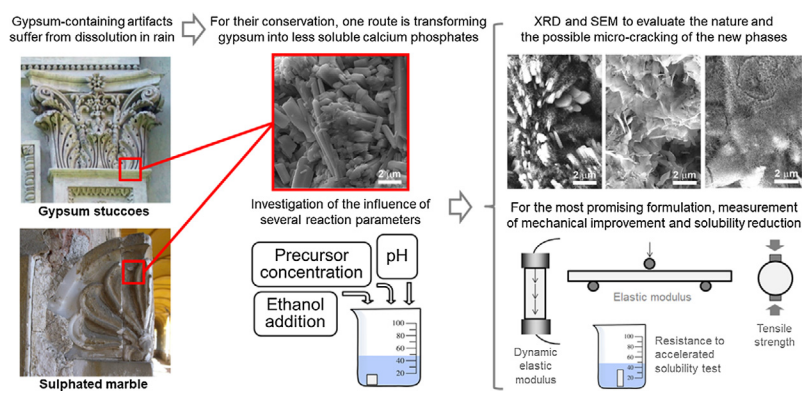
Enrico Sassoni [a,*], Gabriela Graziani [a], Elisa Franzoni [a], George W. Scherer [b]

[a] Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Via Terracini 28, 40131 Bologna, Italy
[b] Department of Civil and Environmental Engineering (CEE), Princeton University, 69 Olden Street, 08542 Princeton NJ, USA

HIGHLIGHTS

- Gypsum treated with phosphate solution is transformed into calcium phosphates (CaP).
- Influence of reaction parameters on CaP nature, morphology and cracking was studied.
- Treated gypsum pastes showed increased mechanical properties and reduced solubility.
- Phosphate treatment gave better results than treatment with ammonium oxalate (AmOx).
- Phosphate treatment showed higher penetration depth than AmOx, but still limited.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 September 2017
Received in revised form 9 February 2018
Accepted 8 March 2018
Available online 23 March 2018

Keywords:
Hydroxyapatite
Brushite
Gypsum
Marble
Solubility
Consolidation
Protection
Acid rain
Cultural heritage
Stucco

ABSTRACT

To increase the water resistance of gypsum-based stuccoes (i.e., pastes and mortars), the possible conversion of gypsum into less soluble calcium phosphates (CaP), by reaction with an aqueous solution of diammonium hydrogen phosphate (DAP), was investigated. The effect of several reaction parameters (DAP concentration, ethanol addition to the DAP solution, pH) on nature and morphology of the new CaP was explored. For the most promising formulation, the ability to improve mechanical properties and reduce solubility in water of treated stuccoes was investigated. The treatment provided better results than ammonium oxalate (an inorganic treatment frequently used for consolidation, protection and de-sulphation of carbonate stones), but the high reaction speed limited the penetration depth and the performance of the DAP-treatment.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Pastes and mortars based on gypsum ($CaSO_4{\cdot}2H_2O$), formed from the reaction between the binder bassanite ($CaSO_4{\cdot}1/2H_2O$) and water, have been used since ancient times to create plasters, renders and bedding mortars. The so-called stuccoes (i.e. pastes

* Corresponding author.
E-mail address: enrico.sassoni2@unibo.it (E. Sassoni).

https://doi.org/10.1016/j.conbuildmat.2018.03.075
0950-0618/© 2018 Elsevier Ltd. All rights reserved.

and mortars molded to create decorative elements) have been used to imitate white and colored marbles, when the supply of real stones from distant quarries was too costly [1].

Because of the high solubility of gypsum in water (~2.5 g/l), decorative elements exposed to rain, rising damp or water vapor condensation may undergo progressive dissolution, leading to surface recession and pulverization [2]. Fig. 1 illustrates some examples of gypsum decorations severely weathered because of their exposure to rain and/or rising damp.

At the time of gypsum stucco creation, it was common practice to add several types of organic additives to the stucco recipes, with the aim of increasing their durability. Sugars, glycerin and citric acid were added to reduce solubility in water [3], while animal blood, egg whites and casein were added to achieve water-repellency [4–6]. Currently, protectives and consolidants are often used. However, commercial treatments (such as ethyl silicate and organic polymers) have exhibited serious limitations when applied to gypsum stuccoes [7]. Ethyl silicate provides little mechanical strengthening, because of the poor bonding between the substrate and the amorphous silica coating, which is affected by diffused cracking; organic polymers exhibit low penetration depth, thus creating a surface layer blocking the pores and negatively altering the water permeability [7]. For these reasons, innovative solutions are needed.

A novel route to preserve gypsum-based elements is converting gypsum into less soluble calcium phosphates (CaP), by treatment with an aqueous solution of diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$). Transforming gypsum into a different mineral might raise concerns in the field of cultural heritage conservation, where very strict requirements about authenticity apply [8]. However, because preserving an artifact by using the same type of mineral is not always feasible and/or effective, conservation of architectural heritage by formation of minerals possibly different from the original ones is commonly accepted and performed in practice. For instance, amorphous silica and polymers (formed by silicate and organic consolidants, respectively) are currently used for conservation of gypsum stuccoes in spite of the above-mentioned limitations of these treatments. Therefore, the compatibility requirement is often interpreted as allowing a treatment that does not have negative consequences on the original substrate [9], which is expected to be the case of phosphate treatment aimed at transforming gypsum into calcium phosphates.

The reaction between gypsum and DAP solutions has been explored in different fields (e.g., biomaterials [10] and building materials [11,12]) and different chemical reactions have been proposed to describe the gypsum transformation:

$$10CaSO_4 \cdot 2H_2O + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6(NH_4)_2SO_4 + 4H_2SO_4 + 18H_2O[10]; \quad (1)$$

$$10CaSO_4 \cdot 2H_2O + 10(NH_4)_2HPO_4 + OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 10(NH_4)_2SO_4 + H_2O + 4HPO^-_{2\,(aq)}[12]; \quad (2)$$

$$5CaSO_4 \cdot 2H_2O + 3(NH_4)_2HPO_4 + 4NH_3 \rightarrow Ca_5(PO_4)_3(OH) + 5(NH_4)_2SO_4 + H_2O[11]; \quad (3)$$

or

$$CaSO_4 \cdot 2H_2O + (NH_4)_2HPO_4 \rightarrow CaHPO_4 \cdot 2H_2O + (NH_4)_2SO_4[11] \quad (4)$$

According to reactions (1)–(3), hydroxyapatite (HAP, $Ca_5(PO_4)_3(OH)$) should form. HAP is usually written as $Ca_{10}(PO_4)_6(OH)_2$, to denote that the crystal unit cell comprises two formula units. Having a dissolution rate in water about 4 orders of magnitude lower than gypsum and being the most stable calcium phosphate [13–15], HAP is the most desirable phase to form. However, in several studies, formation of HAP starting from gypsum was reported to be associated with diffused cracking [10,11], most probably caused by shrinkage during drying [11]. Cracking is undesired, as it can reduce the performance of the HAP layer and even lead to its partial detachment and separation [12]. Alongside HAP [11,12] or even instead of HAP [16], other CaP phases have been reported to form, such as brushite ($CaHPO_4{\cdot}2H_2O$, predicted by reaction (4)) and octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4{\cdot}5H_2O$).

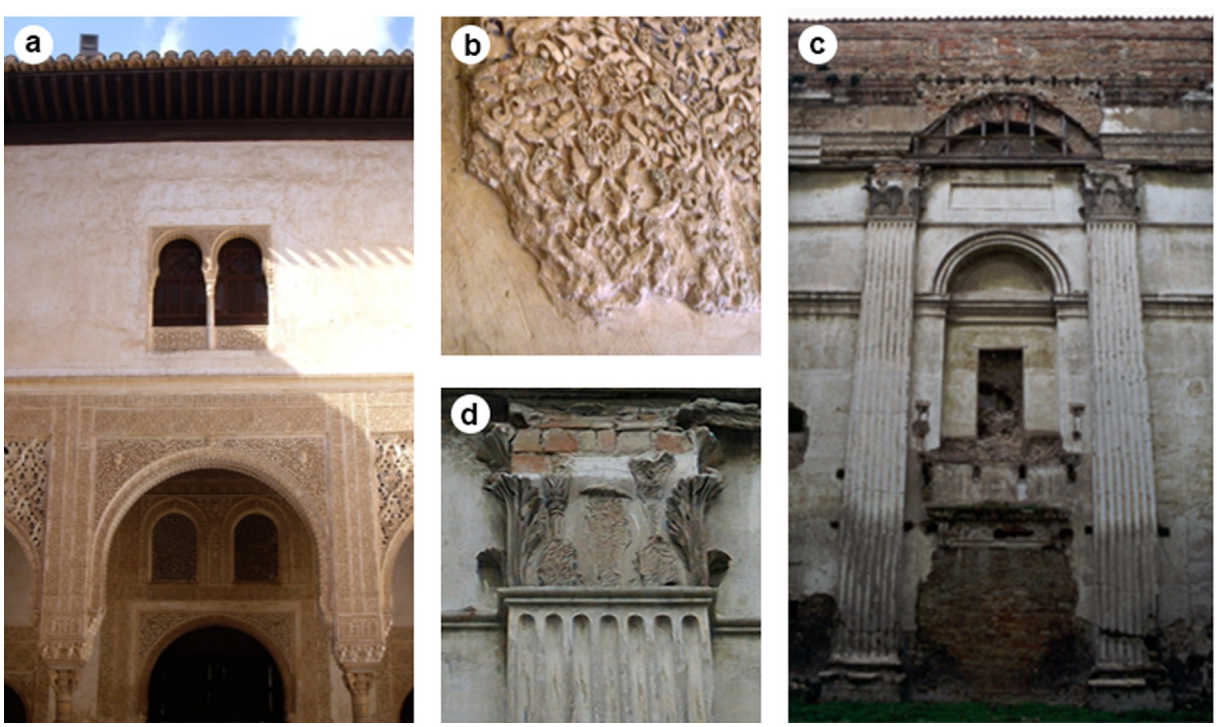


Fig. 1. Examples of weathered gypsum decorations: (a and b) decorations in the Alhambra Palace in Granada (Spain, XIV century) exposed to rain; (c and d) stuccoes in the church of San Francesco in Fano (Italy, XIX cent.) exposed to rising damp from the ground and rain (because of the collapse of the church roof).

Download English Version:

https://daneshyari.com/en/article/6714155

Download Persian Version:

https://daneshyari.com/article/6714155

Daneshyari.com