CONVERSION OF CALCIUM SULFATE DIHYDRATE INTO CALCIUM PHOSPHATES AS A ROUTE FOR CONSERVATION OF GYPSUM STUCCOES AND SULFATED MARBLE

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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.

KEYWORDS

Hydroxyapatite; Brushite; Gypsum; Marble; Solubility; Consolidation; Protection; Acid rain; Cultural Heritage; Stucco

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 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]. Figure 1 illustrates some examples of gypsum decorations severely weathered because of their exposure to rain and/or rising damp.
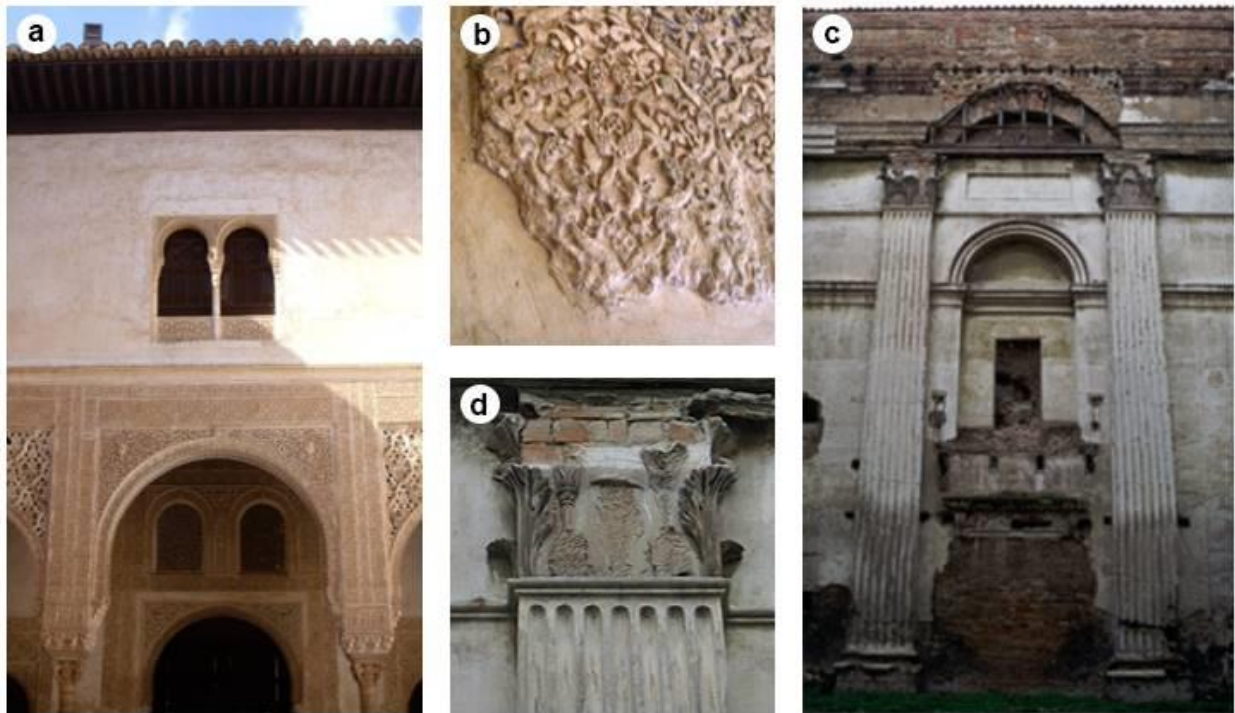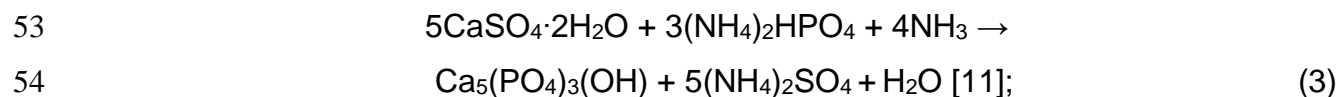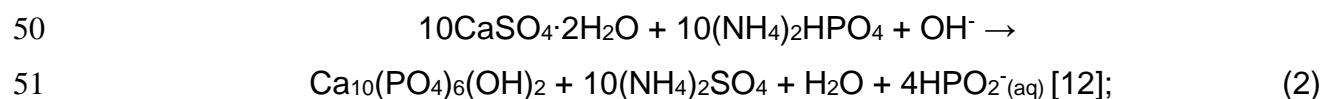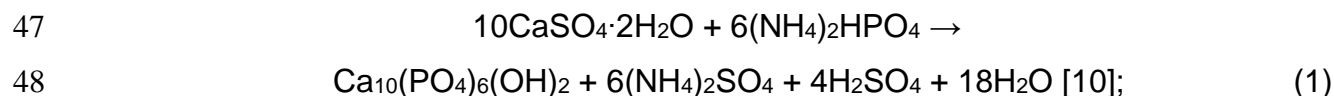

Figure 1. Examples of weathered gypsum decorations: (a,b) decorations in the Alhambra Palace in Granada (Spain, XIV century) exposed to rain; (c,d) stuccoes in the church of San Francesco in Fano (Italy, XIX cent.) exposed to rising damp from the ground and rain (because of the collapse of the church roof).
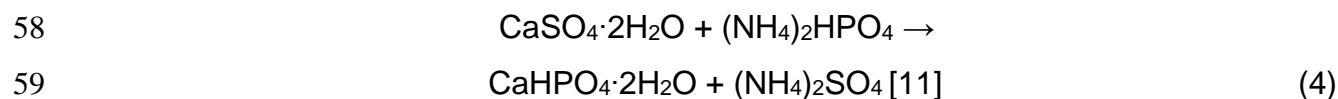
18   At the time of gypsum stucco creation, it was common practice to add several types of

19   organic additives to the stucco recipes, with the aim of increasing their durability.

20   Sugars, glycerin and citric acid were added to reduce solubility in water [3], while animal

21   blood, egg whites and casein were added to achieve water-repellency [4-6]. Currently,

22   protectives and consolidants are often used. However, commercial treatments (such as

23   ethyl silicate and organic polymers) have exhibited serious limitations when applied to

24   gypsum stuccoes [7]. Ethyl silicate provides little mechanical strengthening, because of

25   the poor bonding between the substrate and the amorphous silica coating, which is

26   affected by diffused cracking; organic polymers exhibit low penetration depth, thus

27   creating a surface layer blocking the pores and negatively altering the water

28   permeability [7]. For these reasons, innovative solutions are needed.

29   A novel route to preserve gypsum-based elements is converting gypsum into less

30   soluble calcium phosphates (CaP), by treatment with an aqueous solution of

31   diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$). Transforming gypsum into a

32   different mineral might raise concerns in the field of cultural heritage conservation,

33   where very strict requirements about authenticity apply [8]. However, because

34   preserving an artifact by using the same type of mineral is not always feasible and/or

35   effective, conservation of architectural heritage by formation of minerals possibly

36   different from the original ones is commonly accepted and performed in practice. For

37   instance, amorphous silica and polymers (formed by silicate and organic consolidants,

38   respectively) are currently used for conservation of gypsum stuccoes in spite of the

39   above-mentioned limitations of these treatments. Therefore, the compatibility

40   requirement is often interpreted as allowing a treatment that does not have negative

41   consequences on the original substrate [9], which is expected to be the case of

42   phosphate treatment aimed at transforming gypsum into calcium phosphates.

43   The reaction between gypsum and DAP solutions has been explored in different fields

44   (e.g., biomaterials [10] and building materials [11,12]) and different chemical reactions

45   have been proposed to describe the gypsum transformation:

46

47
$$10CaSO_4 \cdot 2H_2O + 6(NH_4)_2HPO_4 \rightarrow$$

48
$$Ca_{10}(PO_4)_6(OH)_2 + 6(NH_4)_2SO_4 + 4H_2SO_4 + 18H_2O \text{ [10];}$$ (1)

49

50
$$10CaSO_4 \cdot 2H_2O + 10(NH_4)_2HPO_4 + OH^- \rightarrow$$

51
$$Ca_{10}(PO_4)_6(OH)_2 + 10(NH_4)_2SO_4 + H_2O + 4HPO_2^-{}_{(aq)} \text{ [12];}$$ (2)

52

53
$$5CaSO_4 \cdot 2H_2O + 3(NH_4)_2HPO_4 + 4NH_3 \rightarrow$$

54
$$Ca_5(PO_4)_3(OH) + 5(NH_4)_2SO_4 + H_2O \text{ [11];}$$ (3)

55

56 or

57

58
$$CaSO_4 \cdot 2H_2O + (NH_4)_2HPO_4 \rightarrow$$

59
$$CaHPO_4 \cdot 2H_2O + (NH_4)_2SO_4 \text{ [11]}$$ (4)

60

61 According to reactions 1-3, hydroxyapatite (HAP, $Ca_5(PO_4)_3(OH)$) should form. HAP is

62 usually written as $Ca_{10}(PO_4)_6(OH)_2$, to denote that the crystal unit cell comprises two

63 formula units. Having a dissolution rate in water about 4 orders of magnitude lower than

64 gypsum and being the most stable calcium phosphate [13-15], HAP is the most

65 desirable phase to form. However, in several studies, formation of HAP starting from

66 gypsum was reported to be associated with diffused cracking [10,11], most probably

67 caused by shrinkage during drying [11]. Cracking is undesired, as it can reduce the

68 performance of the HAP layer and even lead to its partial detachment and separation

69 [12]. Alongside HAP [11,12] or even instead of HAP [16], other CaP phases have been

70 reported to form, such as brushite ($CaHPO_4 \cdot 2H_2O$, predicted by reaction 4) and

71 octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$). A list of CaP phases and their

72 respective properties is reported in Table 1; for comparison, the solubility of gypsum is

73 2.5-3.1 g/L [17]. These CaP phases have solubility in water higher than HAP, but still

74 much lower than gypsum [15], hence their formation is expected to be beneficial, as

75 long as cracking is prevented. According to reactions 1-3, ammonium sulfate

76 ((NH_4)$_2SO_4$) is also expected to form as a by-product. Being highly soluble in water,

77　　ammonium sulfate is expected to be removed by washing with water, as demonstrated

78　　experimentally [11,12].

79

Abbreviation	Name	Formula	Ca/P ratio	Solubility at 25 °C [g/L]
HAP	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	1.67	~0.0003
CDHA	Calcium-deficient HAP	$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ $(0<x<1)$	1.5-1.67	~0.0094
ACP	Amorphous calcium phosphate	$Ca_xH_y(PO_4)_z \cdot nH_2O$ (n=3-4.5, 15-20% H_2O)	1.2-2.2	n.a.
β-TCP	β-Tricalcium phosphate (or calcium phosphate tribasic)	$\beta\text{-}Ca_3(PO_4)_2$	1.5	~0.0005
OCP	Octacalcium phosphate	$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$	1.33	~0.0081
DCPD	Dicalcium phosphate dihydrate (or brushite)	$CaHPO_4 \cdot 2H_2O$	1.0	~0.088
DCPA	Dicalcium phosphate anhydrous (or monetite)	$CaHPO_4$	1.0	~0.0048
MCPM	Monocalcium phosphate monohydrate	$Ca(HPO4)_2 \cdot H_2O$	0.5	~18
MCPA	Monocalcium phosphate anhydrous (or calcium phosphate monobasic)	$Ca(HPO_4)_2$	0.5	~17
-	Gypsum	$CaSO_4 \cdot 2H_2O$	-	~2.5

80　　**Table 1**. Name, abbreviation, formula, Ca/P, solubility of different CaP phases and gypsum [15].

81

82　　In a previous preliminary study, we found that reacting specimens of gypsum pastes

83　　with a 1 M DAP solution led to the formation of brushite, as well as ammonium sulfate

84　　and koktaite ($(NH_4)_2Ca(SO_4)_2 \cdot H_2O$) as by-products [16]. A possible reason why only

85　　brushite was formed, and not HAP (as would be expected based on the chemical

86　　reactions reported above), may be the lowering of pH during the reaction (according to

87　　reaction 1, H_2SO_4 should form). If pH decreases below 4, formation of brushite is

88　　expected, as this phase is the most stable at pH < 4 [18,19]. Alongside ammonium

89　　sulfate, the formation of koktaite as a by-product is thought to result from the high

90　　amount of calcium ions in the solution, originating from the high solubility of gypsum in

91　　water [16].

92

93   In light of the above reported studies, the aims of the present paper are the following:

94   1) to study the influence of several reaction parameters (viz., concentration of the DAP
95   solution, addition of ethanol, pH of the DAP solution) on the nature and the
96   morphology of the new CaP phases, and to optimize the treatment by promoting
97   formation of phases with low solubility and preventing cracking;

98   2) for the most promising formulation, to test the improvement in mechanical properties
99   and the reduction in solubility of gypsum stuccoes resulting from the formation of the
100   new CaP phases;

101   3) to compare the performance of the most promising formulation of the phosphate
102   treatment with that of ammonium oxalate. The ammonium oxalate treatment was
103   proposed in the 90s for protection of carbonate stones and wall paintings and for
104   desulfation of sulfated substrates [11,20,21]. This latter action can be achieved by
105   transforming gypsum into less soluble calcium oxalate, according to the reaction:

106    $$CaSO_4 \cdot 2H_2O + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 \cdot 2H_2O + (NH_4)_2SO_4 + H_2O. \qquad (4)$$
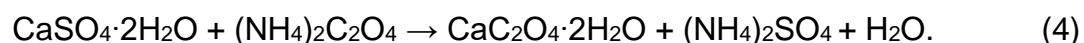
107   The consolidating ability of the oxalate treatment on gypsum stuccoes was here
108   investigated because a good mechanical improvement has been reported in the
109   case of sugaring marble [21], even if a poor performance has been found in other
110   studies [15] (so that new routes for improving the treatment based on calcium
111   oxalate are currently being investigated [22]).

112   Moreover, based on the results obtained on gypsum stuccoes, the suitability of using
113   the same formulation of the phosphate treatment also for conservation of sulfated
114   marble was preliminarily investigated. The use of DAP solutions for marble protection
115   [23-26] and consolidation [15,27-29] has been studied in the last few years with very
116   encouraging results. However, the cited studies have been carried out on
117   uncontaminated marble samples, whereas marble in the field is often covered with a
118   layer of gypsum. This gypsum layer is the result of the reaction between marble and
119   sulfur dioxide, which was present in the atmosphere in high concentrations in the past
120   decades, before traffic regulation policies led to the current low values [30], and which is
121   still present in places where such regulations have not been established yet. Some pilot

122   applications of the DAP-based treatment onto naturally decayed stones (exhibiting

123   gypsum contamination) have shown that the presence of gypsum can significantly alter

124   the composition of the CaP phases formed after treatment [15,31]. Therefore, in the

125   present study, a preliminary evaluation of the treatment effect on sulfated marble was

126   carried out, in terms of morphology and composition of the new CaP phases formed

127   after treatment. It is noteworthy that, in the case of sulfated marble, the possible pH

128   decrease during the reaction (where, according to reaction 1, H_2SO_4 may form) is

129   potentially a major issue, because it might cause severe aggression to marble

130   underlying the gypsum layer. Therefore, the variation in pH during treatment of sulfated

131   marble with the DAP solution was carefully monitored.

132

133 2. MATERIALS AND METHODS

134 2.1. Materials

135   *2.1.1. Gypsum stuccoes*

136   To simulate ancient stuccoes, specimens of gypsum pastes (with no aggregates) were

137   prepared starting from bassanite (the so-called "*scagliola*"), supplied by Gessificio Prioli

138   srl, Italy (purity ~95%). Bassanite was mixed with water (water/bassanite weight ratio of

139   0.5) and prismatic specimens ($4 \times 4 \times 16$ cm^3) were cast. After hardening, the specimens

140   were sawn to obtain cubic (1 cm edge length), cylindrical (2 cm diameter, 4 cm height)

141   and prismatic samples ($1 \times 1 \times 16$ cm^3).

142   *2.1.2. Sulfated marble*

143   To simulate sulfated marble, cubic specimens (1 cm edge length) of Carrara marble

144   (BasketweaveMosaics.com, USA) were immersed in an aqueous solution of H_2SO_4

145   (Sigma Aldrich) at pH 2 for 24 hours. In this way, a surface layer of gypsum was formed

146   over the marble substrate.

147   *2.1.3. Chemicals*

148   Diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$, assay > 99%, Sigma Aldrich),

149   ammonium oxalate $((NH_4)_2C_2O_4 \cdot H_2O$, assay > 99%, Sigma Aldrich), calcium chloride

150    $(CaCl_2 \cdot 2H_2O$, assay > 99%, Sigma Aldrich), ammonium hydroxide (ACS Grade),

151   ethanol (Fisher-Scientific) and deionized water were used.

152   **2.2.   Treatments**

153   A scheme summarizing the various treatment conditions and the respective specimens

154   is reported in Figure 2.

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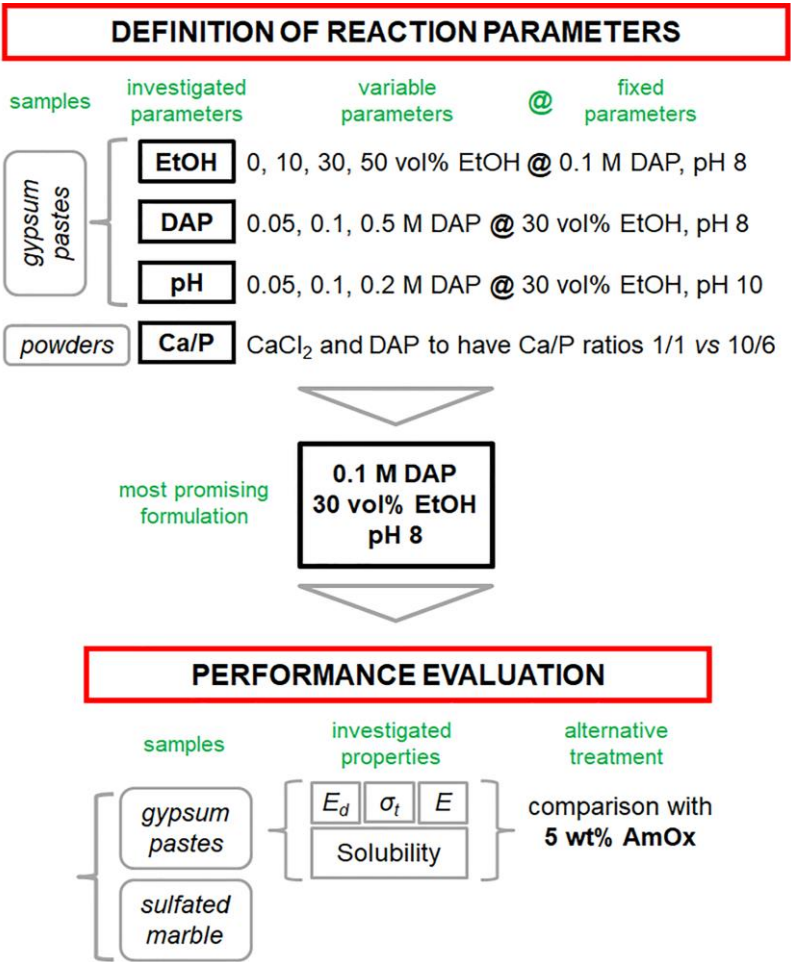
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157   **Figure 2**. Scheme illustrating the various treatment conditions and specimens.

158   *2.2.1. Phosphate treatment*

159   Apart from the role of the Ca/P ratio (investigated as described in the following), the

160   influence of all the other parameters was tested by immersing specimens of gypsum

161   stuccoes (1 cm cubes) in 200 ml of DAP solution for 24 hours. The variation in pH of the

162   DAP solution was monitored during the 24-hour reaction. At the end of the treatment,

163   samples were abundantly rinsed with water and then dried at room temperature. The

164   following parameters were considered:

165   ➢ ethanol concentration. A previous study had shown that the undesired, soluble

166   phase koktaite was formed when samples of gypsum stuccoes were reacted with a 1

167   M DAP solution [16]. The formation of this phase was ascribed to an excess of

168   calcium ions available in the DAP solution, as a result of the high solubility of

169   gypsum in water. Consequently, a reduction in the solubility of gypsum in the DAP

170   solution (and hence a reduction in the free calcium ions) appears as a promising

171   route to prevent the formation of koktaite. According to the literature, a reduction in

172   gypsum solubility in aqueous solutions can be achieved by adding ethanol to water:

173   a 30 wt% addition of ethanol to water was found to reduce gypsum solubility by

174   about 30% [32]. Consequently, ethanol additions of 0, 10, 30 and 50 vol% to a 0.1 M

175   aqueous DAP solution were here investigated. A DAP concentration of 0.1 M was

176   selected (instead of the higher concentrations previously tested in the literature,

177   namely 1 M [16], 3 M [12] and 3.8 M [11]) because studies on marble showed that

178   the addition of ethanol to the DAP solution provides a continuous, crack-free and

179   pore-free film, using only millimolar concentrations of DAP. This is possible thanks to

180   the boosting effect that ethanol has on the reactivity of phosphate ions in the solution

181   [25,29].

182   ➢ DAP concentration. For the ethanol concentration that showed the best results (30

183   vol%, cf. § 3.1), the effects of higher and lower DAP concentrations were

184   investigated. Samples were reacted in 0.05, 0.1 and 0.5 M DAP solutions, in all

185   cases containing 30 vol% ethanol.

186   ➢ pH of the DAP solution. Without any pH modification, a 0.1 M DAP solution has pH

187   8. However, at higher pH a higher amount of PO_4^{3-} ions (necessary to form HAP) is

188   expected to form from DAP dissociation [24,33]. Therefore, the effect of increasing

189   the pH of the DAP solution from 8 to 10 was investigated. Solutions with increasing

190   DAP concentration (0.05, 0.1 and 0.2 M, the latter being the maximum concentration

191   not leading to immediate precipitation at pH 10) were explored, at a constant ethanol

192   concentration of 30 vol% and pH 10. The pH was adjusted using ammonium

193   hydroxide, which was selected among possible bases because it leaves no

194   undesired cations in the solution.

195   ➢ Ca/P ratio. To study the influence of the starting Ca/P ratio on the composition of the

196   new CaP phases, a simplified system was considered. Two aqueous solutions with

197   different Ca/P ratios were prepared. DAP was added to a 10 mM aqueous solution

198   of $CaCl_2 \cdot 2H_2O$ in such an amount to obtain (i) a Ca/P ratio of 10/6 (corresponding to

199   that of HAP) and (ii) a Ca/P ratio of 1/1 (corresponding to that of brushite). In both

200   cases, the precipitate was filtered, dried at room temperature and then analyzed by

201   powder X-ray diffraction (XRD), using a Rigaku MiniFlex diffractometer (detector

202   scan range 2θ=3-60°, step size = 0.04 θ, step time = 0.8 s, kV = 40, mA = 40).

203   *2.2.2. Oxalate treatment*

204   For comparison's sake, specimens of gypsum stuccoes were also treated by immersion

205   in a 5 wt% aqueous solution of ammonium oxalate for 24 hours. At the end of the

206   treatment, samples were abundantly rinsed with water and then dried at room

207   temperature.

208   **2.3.   Characterization**

209   *2.3.1. Nature and morphology of the new CaP phases*

210   The mineralogical composition of the new CaP phases formed on the surface of treated

211   samples (1 cm cubes) was determined by grazing incidence diffractometry (GID), using

212   a Bruker D8 Discover X-Ray Diffractometer (incidence radiation θ=0.5°, detector scan

213   range 2θ=3-37°, step size = 0.02 θ, step time = 0.4 s, kV = 40, mA = 40). Thanks to the

214   low penetration depth of the incoming radiation (a few hundreds of nanometers from the

215   surface), by GID it is possible to determine the composition of the surface layers without

216   interference from the substrate. The same technique was used also for checking the

217   formation of gypsum after the preliminary accelerated sulfation procedure carried out on

218   marble samples (cf. § 2.1.2).

219   The morphology and the possible presence of cracks in the new CaP phases formed

220   after treatment was assessed by observation with an environmental scanning electron

221   microscope (FEI Quanta 200 FEG ESEM) equipped with an energy dispersive x-ray

222   spectroscopy device (Oxford Instruments EDS probe). Before ESEM observation,

223   samples were made conductive by coating with carbon. The same instrument was used

224   also for observing the gypsum layer formed after accelerated sulfation of marble

225   samples (cf. § 2.1.2).

226   *2.3.2. Mechanical properties*

227   The improvement in mechanical properties of the gypsum stuccoes after consolidation

228   was evaluated for (i) the phosphate treatment based on 0.1 M DAP with 30 vol%

229   ethanol at pH 8 (labeled "DAP") and (ii) for the ammonium oxalate treatment (labeled

230   "AmOx"). The mechanical improvement was evaluated in terms of:

231   ➢ dynamic elastic modulus (E_d). E_d can be determined non-destructively by measuring

232   the time required by an ultrasonic pulse to cross the sample. Being a non-destructive

233   test, it can be repeated on the same sample before and after consolidation. E_d was

234   determined according to the formula $E_d = \rho\, v^2$, where ρ is the density and v is the

235   ultrasonic pulse velocity. v was measured across the 4 cm height of the cylindrical

236   samples by a PUNDIT instrument with 54 kHz transducers, using a rubber couplant

237   to improve the contact. For each condition, 5 samples were tested.

238   ➢ static elastic modulus (E). E was tested because, unlike E_d, it is not affected by the

239   pore-clogging effect that consolidants might have, which could lead to an increase in

240   E_d without necessarily implying an increase in the actual stiffness. E was determined

241   by three-point beam bending, from the slope of the stress-strain curve obtained by

242   loading the 1×1×16 cm^3 samples. Samples were placed on two supports at a

243   distance of 120 mm and then loaded in the center by a pushrod, activated by a

244   stepping motor. The load was measured by a 1 kg load cell, while the deflection was

245   measured by a linear variable displacement transducer (LVDT). *E* was calculated

246   from the slope of the stress-strain curve, determined by linear regression of five

247   stress-strain coordinates. For each condition, 5 samples were tested.

248   ➢   tensile strength (σ_t). σ_t was determined because the tendency of grains to detach

249   from the substrate depends on the material cohesion, which can be evaluated by the

250   splitting test. The same cylindrical samples as for the E_d measurement were used.

251   Samples were loaded along two diametric lines until failure, using an Instron testing

252   machine (loading rate 2 mm/min). This method generates tension in a narrow band

253   between the lines of contact, so it is not much affected by treatments that produce

254   only superficial hardening of the cylinder.

255   *2.3.3. Solubility*

256   The reduction in solubility after treatment was determined by a simplified test. After

257   drying to constant weight, untreated and treated cylindrical samples were immersed in

258   600 ml of deionized water at initial pH 5 (each sample in a different container), water

259   being kept stirring by a magnetic stirrer. After 24 hours, the samples were extracted

260   from water and dried at room temperature until constant weight. The weight loss after

261   prolonged exposure to water was then determined by comparing the initial and the final

262   weights.

263   *2.3.4. Penetration depth*

264   The penetration depth of the phosphate and oxalate treatments was assessed by SEM

265   observation of cross sections obtained by chisel from the cylindrical samples used for

266   the splitting tensile test. After coating with aluminum to make them conductive, the

267   samples were observed using a Philips XL20 SEM equipped with an EDAX EDS probe.

268

269   **3.   RESULTS AND DISCUSSION**

270   **3.1.   Gypsum stuccoes**

271   *3.1.1. Formation of new CaP phases*

272   The effect of the investigated parameters on the mineralogical composition of the new

273   CaP phases is reported in Figure 3, while the morphology of the new phases is

274   illustrated in Figure 4, Figure 5 and Figure 6.
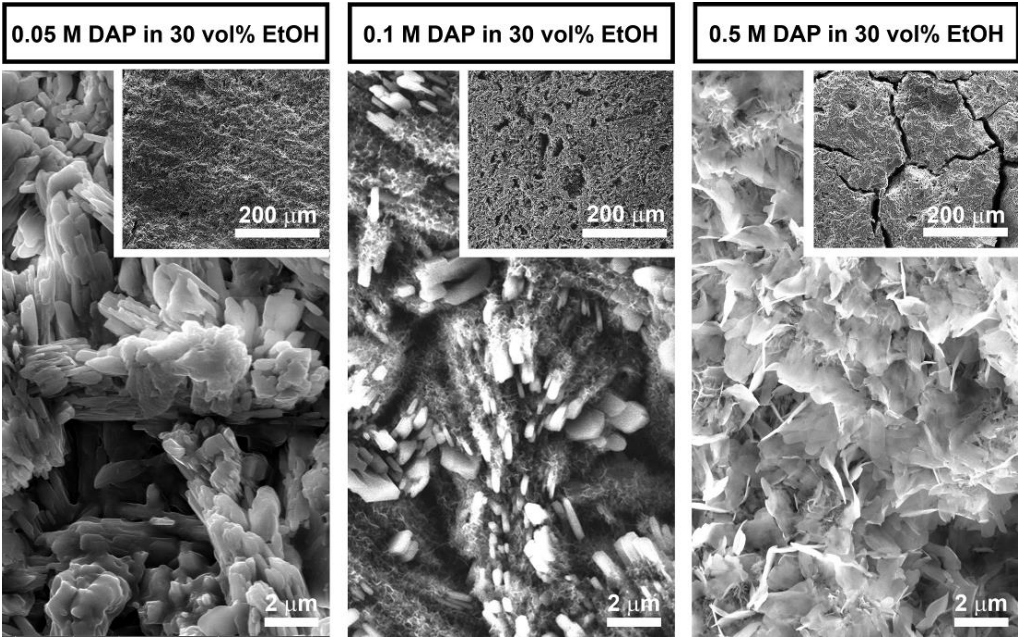

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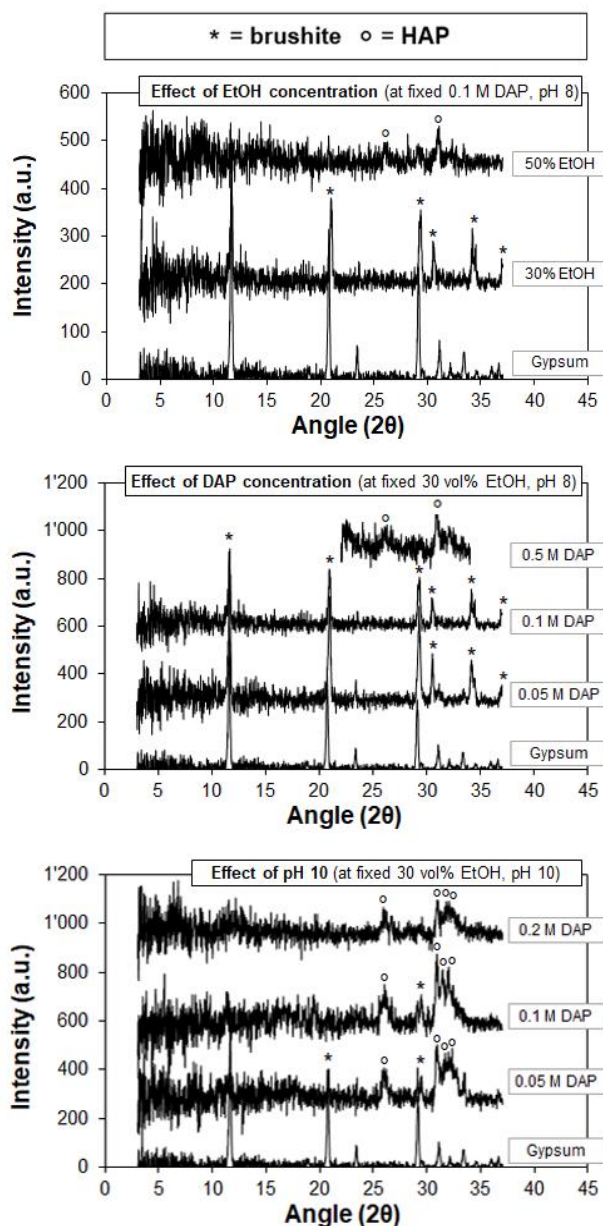
276   **Figure 3**. Mineralogical composition of the new CaP phases formed by treating gypsum

277   samples with different formulations of the phosphate treatment, to investigate the effect of

278   ethanol concentration (top), DAP concentration (medium) and pH increase to 10 at various DAP

279   concentrations (bottom).

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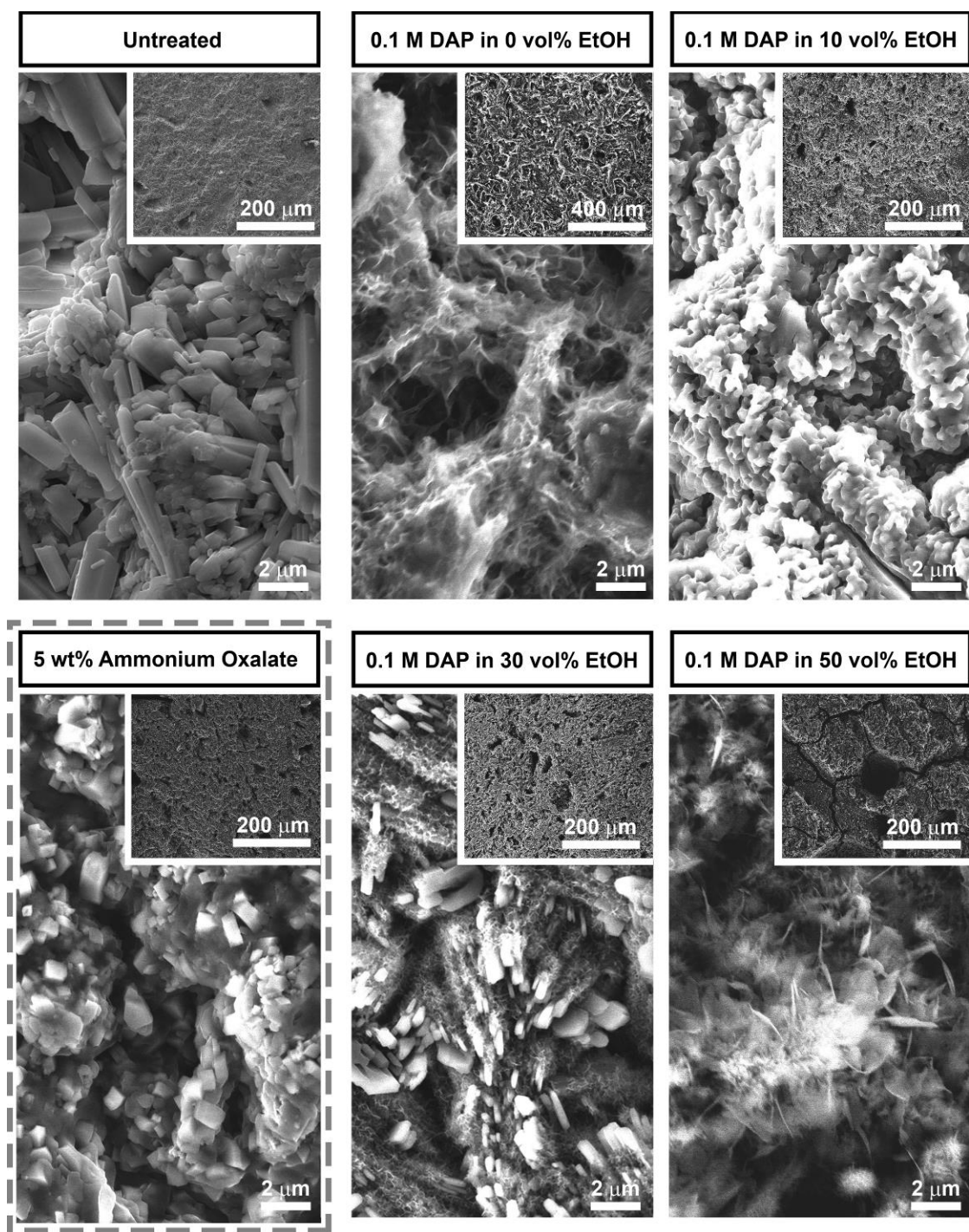
Figure 4. Morphology of the new CaP phases formed by reacting gypsum with different formulations of the phosphate treatment, to investigate the effect of ethanol concentration. For comparison's sake, also the untreated reference and whewellite formed after treatment with ammonium oxalate (dashed box) are reported.

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Figure 5. Morphology of the new CaP phases formed by reacting gypsum with different formulations of the phosphate treatment, to investigate the effect of DAP concentration.
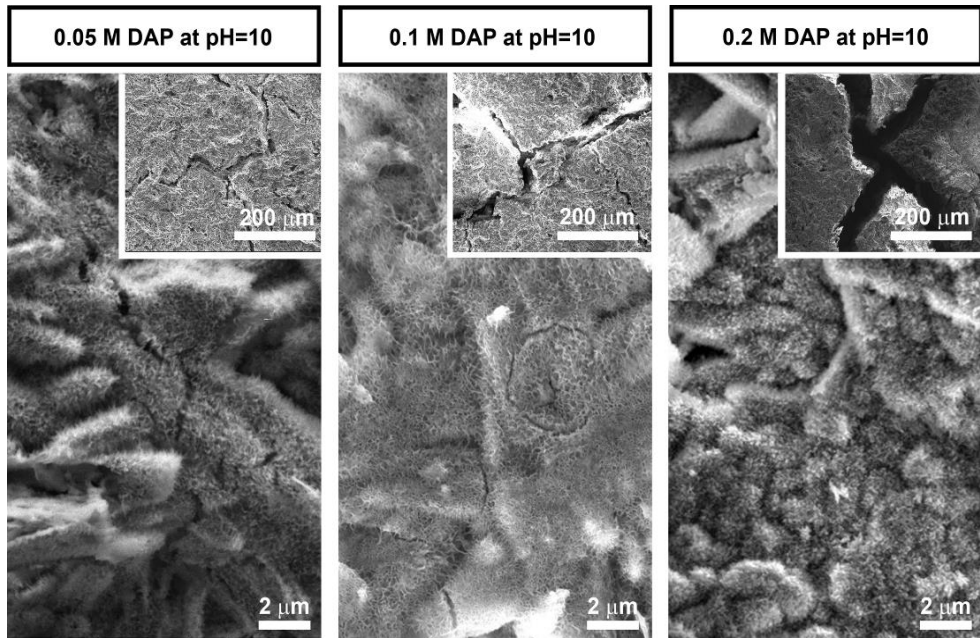
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Figure 6. Morphology of the new CaP phases formed by reacting gypsum with different formulations of the phosphate treatment, to investigate the effect of increasing pH to 10, at various DAP concentrations.

293   After reaction with a 0.1 M DAP solution containing no or 10 vol% ethanol addition,

294   some new CaP phases were formed (Figure 4). They could not be identified by GID,

295   likely because of the very small amount produced. The limited formation of CaP phases

296   when such a low DAP concentration was used is consistent with previous results

297   obtained on fresh marble, where no new phases were observed if no ethanol was

298   added to the 0.1 M DAP solution [29]. In the case of gypsum, when the ethanol

299   concentration was increased to 30 and 50 vol%, abundant new phases were formed,

300   having a clearly different morphology (Figure 4). As reported in Figure 3, the new

301   phases were identified as brushite (30 vol% ethanol) and HAP (50 vol% ethanol). In this

302   latter case, the treated sample exhibited diffused cracking (Figure 4), which is

303   undesirable for achieving protection from dissolution in water.

304   When the effect of increasing the DAP concentration was investigated, the modification

305   in phase composition and morphology reported in Figure 3 and Figure 5, respectively,

306   was obtained. Whereas brushite was the main phase formed at 0.05 and 0.1 M DAP,

307   HAP (exhibiting a clearly different morphology, Figure 5) was formed at 0.5 M DAP.

308   However, also in this case, formation of HAP was associated with heavy cracking of the

309   sample surface, while no cracking was observed in samples where brushite formed

310   (Figure 5).

311   Formation of HAP is expected from reactions 1-3, but in some of the investigated

312   conditions brushite was formed instead of HAP. A possible explanation for this might be

313   the lowering of pH during the reaction as predicted by reaction 1. If pH decreases below

314   4, then brushite would be the most stable CaP phase and hence its formation would be

315   expected [19]. To verify whether this was the case, in all the experiments the pH was

316   monitored. The pH was found to change only slightly during the reaction (from 8.1 to

317   8.0), hence never getting below 4. Therefore, pH variation was excluded as the possible

318   reason why brushite was formed instead of HAP.

319   Another possible explanation could be that brushite (requiring HPO_4^{2-} ions) is kinetically

320   favored over HAP (requiring PO_4^{3-} ions), as DAP speciation leads to a much higher

321   amount of the former ions with respect to the latter. For instance, in the case of a 0.1 M

322   DAP solution (with no ethanol addition), calculations performed with Mathematica®

323   (following the method described in [24]) predict the following concentrations of

324   phosphate ions: 0.0959 M HPO_4^{2-} ions, 0.0039 M $H_2PO_4^-$ ions and only 3.3×10^{-5} M

325   PO_4^{3-} ions, hence a ratio of HPO_4^{2-}/PO_4^{3-} of about 2900. The ratio becomes even higher

326   (about 5850) if an amount of $CaCl_2$ sufficient to match gypsum solubility limit (15.1 mM

327   [34]) is also considered in the solution. The hypothesis that brushite is kinetically

328   favored over HAP would also explain the change in phase composition detected for

329   increasing ethanol concentration or increasing DAP concentration. In fact, in either

330   case, the Ca/P ratio is decreasing (because fewer Ca ions are available and more P

331   ions are available, respectively). Because HAP has a higher Ca/P ratio than brushite

332   (1.67 *vs* 1, respectively), formation of HAP would be expected to be favored at higher

333   Ca concentrations (i.e., lower ethanol concentrations) or at lower DAP concentrations.

334   To verify whether formation of brushite occurs because the kinetics predominates over

335   the effect of the Ca/P ratio, solutions were prepared with different Ca/P ratios, namely

336   10/6 (corresponding to that of HAP) and 1/1 (corresponding to that of brushite) (cf. §

337   2.2.1). As illustrated in Figure 7, in both cases brushite was the main phase that formed,

338   with only minor amounts of HAP. This suggests that, independently of the starting Ca/P

339   ratio, formation of more soluble brushite is favored over less soluble HAP, likely

340   because HPO_4^{2-} ions needed to form brushite are more easily available than PO_4^{3-} ions

341   needed to form HAP. Accordingly, in a recent paper [12] it was proposed that formation

342   of CaP phases follows the Ostwald's rule, i.e. the phase with the fastest precipitation

343   rate is preferentially formed, even if it is not the most stable one [12].
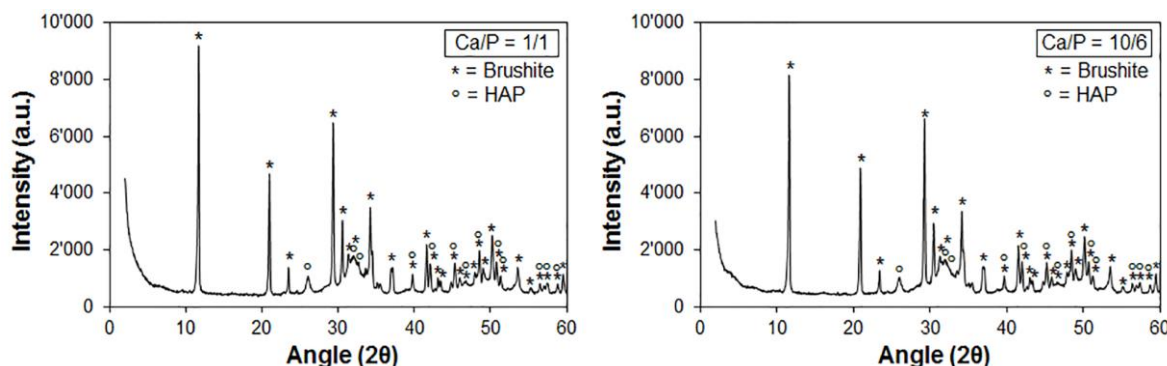
344
345   **Figure 7**. Composition of the new CaP phases precipitated from solutions with Ca/P ratio of 1/1

346   (left) and Ca/P ratio of 10/6 (right).

347   To promote formation of HAP, we increased the pH of the starting DAP solution from 8

348   to 10, because more PO_4^{3-} ions (required to form HAP) are available at higher pH [33].

349   As expected, a significant change in phase composition was achieved by increasing the

350   pH (Figure 3). At low DAP concentrations (0.05 and 0.1 M), brushite was still present,

351   but also HAP was formed. At higher DAP concentration (0.2 M, the highest

352   concentration not leading to direct precipitation at pH 10), only HAP was detected.

353   However, in all cases the new CaP phases exhibited diffused cracking (Figure 6), which

354   presumably occurred during drying because the porous films exceeded the critical

355   thickness for cracking (below the critical thickness, cracking is thermodynamically

356   inhibited [35]). In addition to altering the aesthetic appearance of the treated stuccoes

357   (as they are visible even by naked eye), cracks are expected to be detrimental to

358   protection from dissolution in water. Therefore, formulations at pH 10, leading to

359   diffused cracking, were regarded as not promising for providing satisfactory protection.

360   It is noteworthy that in no case was formation of undesired koktaite [16] detected, which

361   was the aim of adding ethanol to the DAP solution (because ethanol reduces the

362   solubility of gypsum in water [32] and hence the amount of free calcium ions in the DAP

363   solution). Moreover, neither was formation of ammonium sulfate detected by GID, which

364   is the positive result of abundantly washing samples with deionized water at the end of

365   the 24 hour reaction. However, this washing procedure was sufficient to entirely remove

366   ammonium sulfate in the samples used for GID (1 cm cubes), but not in bigger samples

367   used for mechanical tests (e.g. cylinders with 2 cm diameter and 4 cm height). After

368   treatment, washing and drying, the latter samples exhibited some color change towards

369   grey, owing to formation of ammonium sulfate, detected also by GID. However, by

370   further saturating the samples with deionized water by capillary rise and then

371   submerging the samples, ammonium sulphate was almost completely removed, as

372   indicated by GID and by the color change back to the initial one. Accordingly, no traces

373   of nitrogen were detected by SEM/EDS on cross sections obtained from the cylindrical

374   samples used for the tensile strength test.

375   In light of these results, the formulation of the phosphate treatment based on a 0.1 M

376   DAP solution also containing 30 vol% ethanol at pH 8 was considered as the most

377   promising one, as it leads to formation of brushite (significantly less soluble than

378   gypsum, although more soluble than HAP), without cracking. In terms of long term

379   stability, brushite (as well as other metastable CaP phases) are expected to undergo

380   dissolution and reprecipitation processes, finally leading to formation of the most stable

381   CaP phase, i.e. HAP. In the case of a CaP layer formed by reacting gypsum with DAP

382   solutions, progressive densification of the layer with time, thanks to formation of

383   additional CaP phases, was found experimentally [12]. On the contrary, dehydration of

384   brushite to monetite ($CaHPO_4$, having much higher water solubility than brushite, Table

385   1) was not found to occur in practical conditions [11]. Therefore, the long term stability

386   of the so-formed brushite is expected to be satisfactory.

387   The consolidating and protecting ability of the above-reported formulation (labeled

388   "DAP") was hence investigated and compared to that of commercial ammonium oxalate

389   (labeled "AmOx").

390   *3.1.2. Mechanical consolidation*

391   The variations in mechanical properties after application of the phosphate and oxalate

392   treatments are reported in Table 2.

393

|	Untreated	DAP	Variation	AmOx	Variation
E_d (GPa)	9.9 (±0.4)	10.3 (±0.1)	+3%	11.1 (±0.6)	+12%
E (GPa)	4.0 (±0.5)	4.2 (±0.2)	+5%	4.0 (±0.2)	0%
σ_t (MPa)	3.4 (±0.7)	3.8 (±0.2)	+13%	3.3 (±0.6)	-3%
Δw (%)	9.5	7.9	-17%	9.5	0%

394   **Table 2**. Mechanical properties and weight loss after immersion in water of untreated and

395   treated samples (E_d = dynamic elastic modulus; E = static modulus; σ_t = tensile strength; Δw =

396   weight loss). Values of mechanical properties are averages for 5 samples (standard deviations

397   in brackets).

398

399   The DAP treatment caused modest increases in dynamic elastic modulus E_d and static
400   modulus E (+3% and +5%, respectively) and a slightly higher increase in tensile
401   strength (+13%). This limited mechanical improvement seems to derive from the low
402   depth of formation of new CaP phases, as assessed by SEM/EDS analysis of cross
403   sections. As illustrated in Figure 8 and Figure 9, the formation of new CaP phases and
404   the consequent presence of phosphorus are mainly concentrated in the first 50-100 μm
405   from the surface. Traces of new CaP phases were observed at a depth of 500 μm from
406   the surface, while no new phases were detected at 1 mm (Figure 9). This reduced
407   penetration depth, in spite of the ability of the DAP solution to penetrate deeply into
408   porous substrates (up to 25 mm in porous limestone [36-38]), is thought to be a
409   consequence of the fast reaction between the DAP solution and gypsum.
410   Notwithstanding the addition of ethanol to the DAP solution to reduce gypsum solubility,
411   the presence of a large amount of calcium ions available for reaction is responsible for
412   the consumption of phosphate ions in the DAP solution, so that new CaP phases form
413   mostly near the surface. Possible strategies for reducing the reaction speed and hence
414   favor formation of the new CaP phases also in depth are currently under investigation.
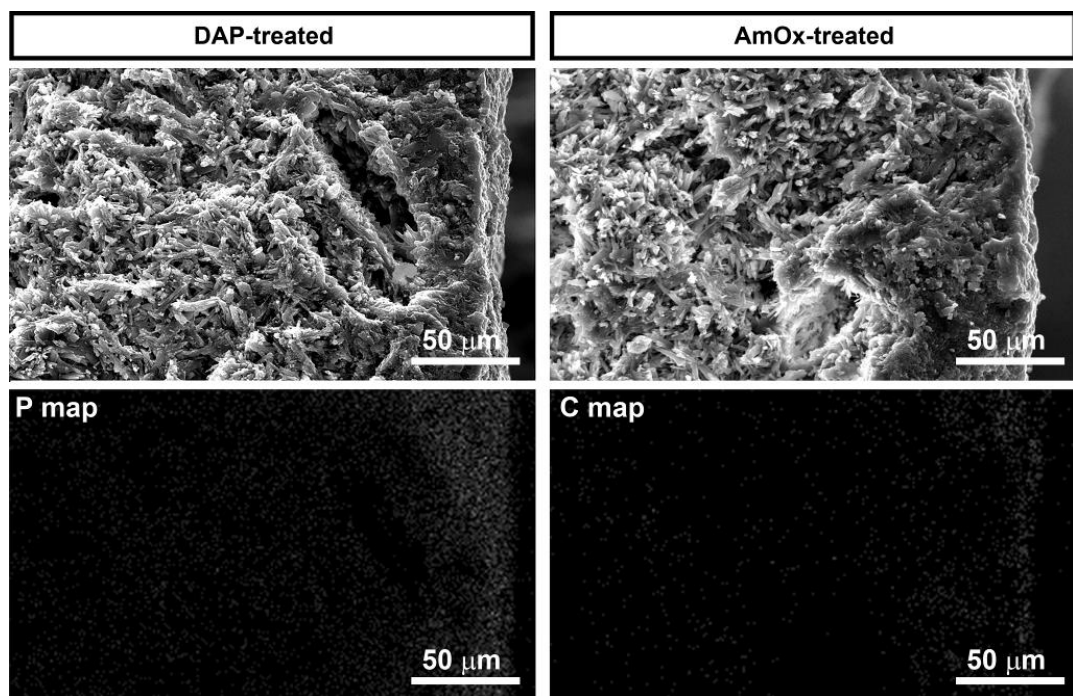
415

416   **Figure 8**. Morphology and elemental maps of cross sections of samples treated by DAP (left)
417   and AmOx (right).

Surface	100 μm depth	500 μm depth	1 mm depth

418
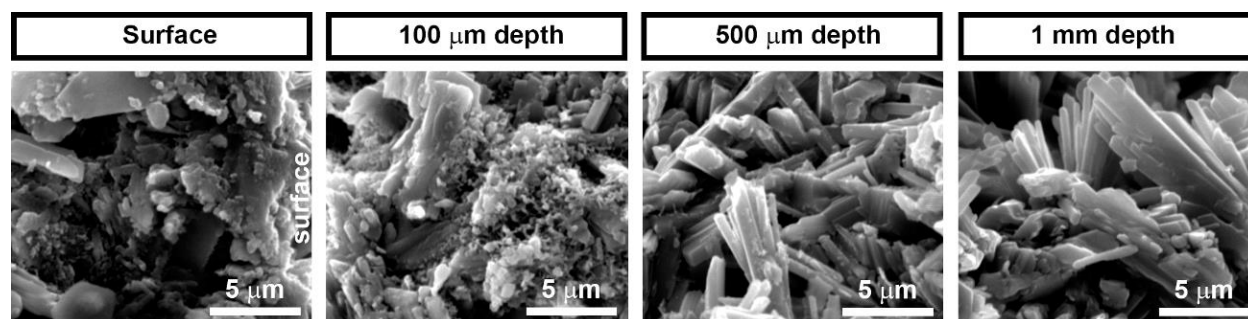
419 **Figure 9**. New CaP phases at increasing depth from the surface. Whereas abundant new

420 phases are present near the surface and can still be clearly observed at 100 μm depth, only

421 minor traces of new CaP phases are visible at 500 μm depth (small flakes formed on the

422 surface of the big gypsum crystals) and no trace is found at 1 mm depth.

423

424 In the case of the AmOx treatment, gypsum was transformed into whewellite

425 ($CaC_2O_4 \cdot H_2O$), as indicated by GID and illustrated in Figure 4 (dashed box). In this

426 case, even if a higher increase in E_d was registered (+12%), no significant increase in

427 either the static modulus or the tensile strength was found (Table 2). The lack of any

428 substantial consolidating action is thought to be a consequence of the reduced depth of

429 formation of whewellite, which in turns derives from the kinetics of reaction between the

430 ammonium oxalate solution and the substrate. As recently pointed out in a study on

431 carbonate stones, ammonium oxalate tends to react with calcite more quickly than DAP,

432 which leads to a lower penetration depth of the former treatment compared to the latter

433 [39]. Accordingly, in the case of gypsum (even more soluble than calcite), in the present

434 study a much lower depth of formation of calcium oxalate was found by SEM/EDS,

435 compared to calcium phosphates (Figure 8). The presence of C (assumed as indicative

436 of formation of whewellite) was detected only at a few tens of microns from the surface.

437 This finding is in agreement with previous results reported in the literature on treatment

438 of gypsum with ammonium oxalate and ammonium phosphate solutions [11]. In the

439 cited study, a strong gradient in the formation of calcium oxalate was reported (the

440 highest amount being concentrated near the surface), whereas a more homogenous

441 formation of CaP phases (present also in depth) was found [11]. The apparent increase

442 in E_d registered in the AmOx-treated samples is thought to derive from formation of

443   ammonium sulfate inside the pores of the samples. In the case of the AmOx treatment,

444   traces of ammonium sulfate were detected by GID even in the 1 cm cubes, although

445   washed at the end of the treatment. In the cylindrical samples used for E_d

446   measurements, while saturation and submersion in water were sufficient to remove

447   basically all the ammonium sulfate from the DAP-treated samples, in the case of the

448   AmOx-treated ones, a considerable amount of ammonium sulfate still remained, as

449   suggested by the color change and confirmed by GID. The difference between the DAP-

450   and the AmOx-treatments in the amount of ammonium sulfate formed inside the pores

451   and remaining after washing derives from the fact that NH_4^+ ions were more abundant in

452   the AmOx solution (about 0.4 M) than in the DAP solution (0.1 M).

453   Comparing the performance of the two treatments, the DAP solution was able to

454   penetrate more in depth and provide greater mechanical improvement than the AmOx

455   treatment, but neither is very effective. Compared to ammonium oxalate, the DAP

456   treatment has the advantage of leading to formation of a smaller amount of ammonium

457   sulfate, that can be more easily removed. For the same reason, even if slightly greater

458   mechanical improvements were found in a previous study where a 1 M DAP solution

459   was used (ΔE_d = +5% and $\Delta\sigma_t$ = +16% [16]), still the formulation adopted in this study

460   seems preferable, considering that the small mechanical advantage had been obtained

461   at the cost of a much higher DAP concentration (10 times as much) and formation of

462   much more ammonium sulfate (and koktaite) inside the sample [16].

463   *3.1.3. Protection from dissolution in water*

464   The results of the simplified dissolution tests are reported in Table 2.

465   In the case of the DAP treatment, thanks to gypsum conversion to brushite, a 17%

466   reduction in weight loss after prolonged exposure to water was registered. The reason

467   why the reduction was not higher (in spite of brushite being about 27 times less soluble

468   than gypsum [15]) is thought to be the porous nature of the brushite layer and of the

469   gypsum substrate, combined with the reduced depth of gypsum conversion to brushite.

470   In fact, porosity allows water to penetrate in depth and reach the inner part of the

471   sample, not completely covered by the newly formed brushite.

472   In the case of the AmOx treatment, no reduction in weight loss was registered,
473   compared to the untreated reference. This is a consequence of the fact that whewellite
474   formed only in the most superficial part of the sample, because of the high speed of the
475   reaction [11]. Combined with the porous nature of the sample, this prevented an
476   effective protecting action from being achieved.

477   **3.2.   Sulfated marble**

478   After immersion in H_2SO_4 at pH 2 for 24 hours, gypsum was formed on the marble
479   surface, as confirmed by GID. The newly formed gypsum exhibited a needle-like
480   morphology, as illustrated in Figure 10.

481

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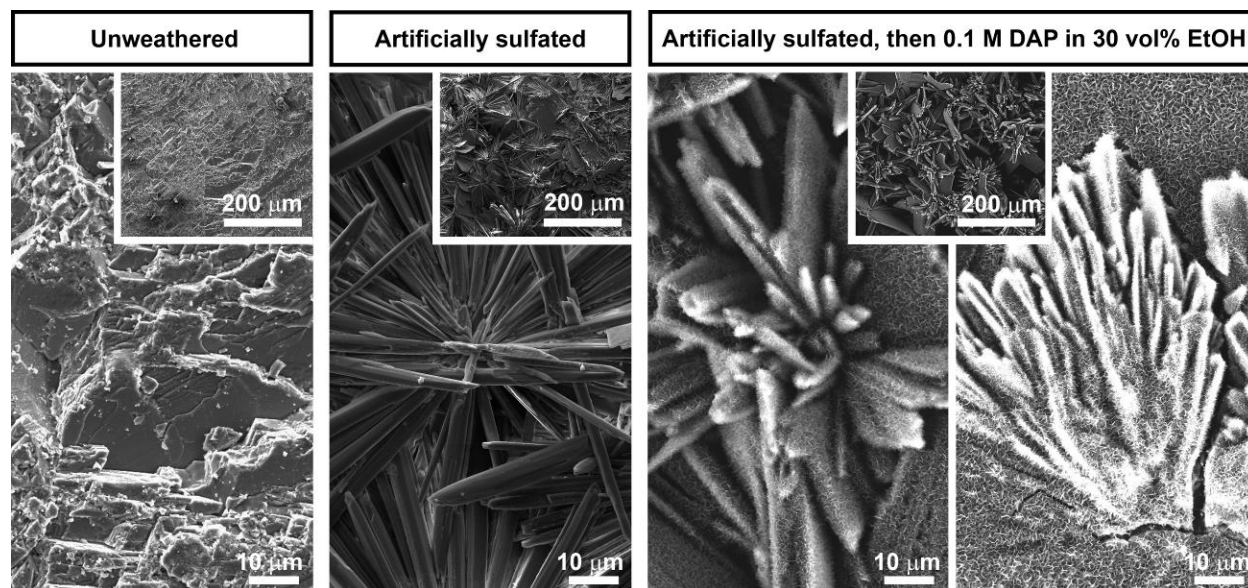
483   **Figure 10**. Morphology of fresh marble (left), artificially sulfated marble (middle) and artificially
484   sulfated marble treated with DAP (right).

485

486   During reaction with the formulation that gave the best results on gypsum stuccoes
487   (namely, a 0.1 M DAP solution in 30 vol% ethanol), the pH of the solution was found to
488   change only slightly, from 8.1 to 8.0. Consequently, no risk of marble corrosion owing to
489   the possible formation of H_2SO_4 during reaction of the gypsum layer with the DAP
490   solution (cf. reaction 1 in § 1) was present.

491   After treatment, new CaP phases were formed, as illustrated in Figure 10. These

492   phases exhibit a morphology more similar to that of HAP (Figure 7) than to brushite

493   (Figure 4), but no conclusive phase identification was achieved by GID. This is probably

494   to be ascribed to the reduced thickness of the new CaP phases, as suggested by the

495   fact that these phases closely follow the morphology of the needle-like gypsum crystals

496   originally covering the marble surface. Whatever the nature of the new CaP phases,

497   their solubility is in any case lower than that of gypsum, hence a benefit in terms of

498   resistance to dissolution is expected.

499   However, some micro-cracks were visible in the CaP layer (Figure 10, right), while no

500   similar cracks were observed in the gypsum layer before treatment with the DAP

501   solution. Because the formation of micro-cracks in the CaP layer may negatively affect

502   its durability, further investigation seems opportune to optimize the treatment outcome

503   in the case of sulfated marble, where the morphology of the starting gypsum crystals

504   may affect the phosphate treatment outcome.

505   It is noteworthy that, in the case of marble covered with gypsum layers embedding dust

506   and particulate matter (the so-called "black crusts"), transformation of gypsum into

507   calcium phosphates would encapsulate the dirt in a layer with reduced solubility, which

508   might be counterproductive. Therefore, whenever possible, the dark matter should be

509   removed by cleaning before application of the DAP-based treatment. Nonetheless, in

510   the case of marble covered by black crusts, below which the marble surface is sugaring

511   (so that cleaning the black crust might threaten the conservation of the underlying

512   marble), preliminary tests we have carried out indicate that the DAP treatment, applied

513   over the gypsum crust, is able to pre-consolidate the marble surface, which becomes

514   able to stand the cleaning operations, while the consolidated crust can still be

515   successfully removed by cleaning.

516   **4. CONCLUSIONS**

517   In the present study, the composition and the morphology of new calcium phosphate

518   phases formed by reacting gypsum pastes with different solutions of diammonium

519   hydrogen phosphate was investigated and the consolidating and protecting ability of the

520   most promising formulation were evaluated. The following conclusions can be derived:

521   1) Formation of phases with low solubility (e.g., HAP) can be obtained by increasing

522   the ethanol concentration (added to reduce gypsum solubility and hence the amount

523   of calcium ions in the solution), by increasing the DAP concentration or by increasing

524   the pH. However, HAP formation was found to be associated with diffused and

525   visible cracking, likely because of excessive growth of the new phase. On the

526   contrary, when more soluble brushite was formed, no cracking was observed.

527   2) Formation of brushite was found to be favored over formation of HAP, likely because

528   brushite requires HPO_4^{2-} ions (by far the most abundant species originated from

529   DAP dissociation) while HAP requires PO_4^{3-} ions (which are present only in very

530   minor amounts). This explains why brushite is preferentially formed, even in a pH

531   range and for a starting Ca/P ratio that should favor HAP.

532   3) Samples of gypsum stuccoes treated for 24 hours with a 0.1 M DAP solution

533   containing 30 vol% ethanol at pH 8 exhibited formation of uncracked brushite. As

534   brushite is less soluble than gypsum (although more soluble than HAP), such

535   treatment caused a 17% decrease in weight loss of the gypsum stuccoes after

536   prolonged exposure to water and a 13% increase in their tensile strength. However,

537   the improvement induced by the phosphate treatment was not as high as hoped

538   because of the reduced depth of formation of brushite, mostly concentrated in the

539   first 50-100 μm from the surface and present only in traces at a depth of 500 μm.

540   The phosphate treatment provided better results than the ammonium oxalate

541   treatment, originally proposed for desulfation of calcareous substrates and here

542   investigated for consolidation and protection of gypsum stuccoes. The performance

543   of the oxalate treatment is mainly limited by the high speed of reaction between the

544   oxalate solution and gypsum, so that the depth of formation of calcium oxalate is

545   only a few tens of microns from the surface. Possible routes to reduce the speed of

546   reaction between the phosphate solution and gypsum are currently under

547   investigation. In the case of the oxalate treatment, use of a lower concentration of

548   ammonium oxalate and/or addition of alcohol might improve the performance, but
549   those variations were not explored in the present study.

550   4) With the aim of treating sulfated marble so as to transform gypsum into less soluble
551   calcium phosphate phases, the same formulation of the phosphate treatment
552   reported above was tested also on artificially sulfated samples of Carrara marble.
553   New calcium phosphate phases with the flower-like morphology typical of HAP were
554   observed, but they could not be identified by GID. Because some cracks were
555   observed in the new calcium phosphate layer, some further optimization of the
556   treatment seems necessary for application to sulfated marble, where the morphology
557   of the gypsum crystals may also play a role.

558 ACKNOWLEDGMENTS

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