



Gypsum crust as a source of calcium for the consolidation of carbonate stones using a calcium phosphate-based consolidant



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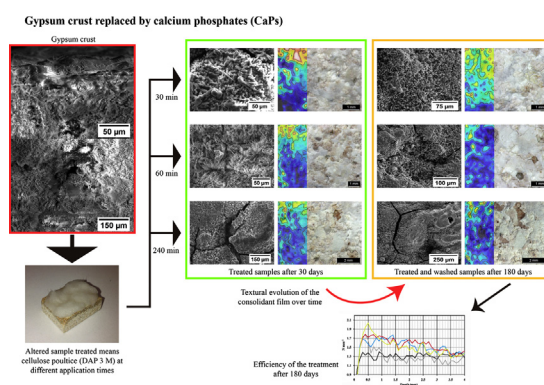
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HIGHLIGHTS

- Treatment to carbonate stones altered by a gypsum crust by dibasic ammonium phosphate.
- Gypsum crust as a source of calcium by calcium phosphate-based consolidant.
- We have assessed the efficacy at different application times means cellulose poultice.
- Application time and water saturation of the poultice affect the amount of gypsum removed.
- Gypsum was eliminated after a single application treated during 60 minutes with DAP.

GRAPHICAL ABSTRACT



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ABSTRACT

The high levels of atmospheric pollution in cities today are causing the decay of natural building stone, especially due to the formation of gypsum crusts on carbonate stones. For this reason we have assessed the efficacy of using the gypsum crust as an alternative source of calcium in the consolidation of building stone via the formation of calcium phosphates. Samples of Arenisca Ronda (southern Spain) were altered to develop a gypsum crust on the surface for subsequent application of a cellulose poultice with a solution of dibasic ammonium phosphate 3 M (DAP) at different application times. The best results were obtained by the samples treated for 60 min and they have indicated that the application time and the water saturation degree of the poultice affect the amount of gypsum removed and the quantity of fissures on the consolidant film. On the other hand, the DAP concentration of the solution and the pH controlled the calcium phosphate precipitation phases. The habit of the calcium phosphate crystals evolve over the time tending to a homogenization of the consolidant film. This procedure offers an important alternative for the treatment of altered carbonate stones, in which the stone can be cleaned and consolidated in a single application.

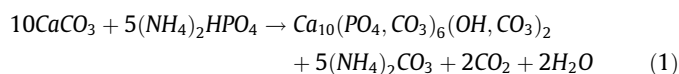
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1. Introduction

Of all the building materials used today and throughout history, natural stone stands out because of its availability in nature, its technical properties and particularly its durability compared to other traditional materials [10]. However, decay is almost inevitable when stone is used in buildings and exposed to often adverse environmental conditions. Research has shown that the speed and the degree of decay of the stone depend on the interaction of a wide range of intrinsic (composition, porosity, texture, etc.) and extrinsic (physical, chemical and/or biological) factors [40]. In addition to these natural factors, there are other anthropogenic factors that significantly enhance decay processes. One of the most obvious is atmospheric pollution in urban areas, where most buildings, monuments and other stone structures are situated [8]. Perhaps the most damaging pollutant is SO_2 which reacts with the carbonated substrate to produce a gypsum crust on the surface of the stone [43]. In addition to the gypsum itself, the crust may also contain other secondary compounds from fossil fuels and/or carbon coal that can act as catalysts in the sulfation reaction [34,35]. This process is a serious problem for the conservation of the historic monuments in any city and also for modern buildings, especially given that in addition to the dirty, causing a decrease of aesthetic value by the blackening of the surface. The crust also causes the stone to decay in a relatively short space of time [5,16,24,29,35,44,46].

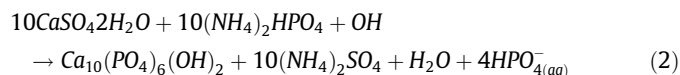
Various techniques have been developed for cleaning the surfaces affected by this problem [25,1,13,18,33]. Moreover the products for consolidating carbonated materials are not as well developed as those for siliceous stones, especially because of the characteristics of the consolidant itself and its degree of compatibility with the stone. In recent years researchers have been assessing the efficacy of the different phases of calcium phosphates and in particular of hydroxyapatite (HAP) as consolidation agents for carbonated stones [36–38,11,21,27,26,28] obtained from the reaction of dibasic ammonium phosphate (DAP) with the calcite according to the following equation:



Calcium phosphates (CaPs) have two main advantages. Firstly, they have no harmful effects on human health and secondly, their low solubility. However, two factors that could have negative effects on the consolidation process and by extension on the material being treated have not been taken into account. Both factors appear in the reaction in equation 1. Firstly, 369 M volumes (V_m) of calcite are needed to produce 159.46 V_m of hydroxyapatite (HAP) and although researchers have tried to cover this need for calcium by adding other calcium compounds, this has resulted in undesirable effects such as excessive growth and cracking of the film [27] or a weakening in the precipitation of the different CaPs [41]. Secondly the release of ammonium ions could enhance the development of microorganisms, as nitrogen is an essential component for living creatures.

In view of this situation, the main objective of this paper is to use the gypsum crust as an alternative source of the calcium required to bring about the precipitation of CaPs and minimize the dissolution of the underlying calcite. This idea of replacing the gypsum with calcium phosphate is not new [2,31,32]. In order to be able to use the gypsum as a source of calcium for the precipitation of the CaPs and to fix the nitrogen, we will be basing our research on an analogy of the Ferroni-Dini method [20] where the authors used ammonium carbonate (instead of DAP) to react with the gypsum, so forming ammonium sulfate.

Our procedure for the cleaning and consolidation of stone using calcium phosphates via the reaction of dibasic ammonium phosphate and gypsum is based on the following equation:



This equation presents the ideal reaction for the formation of hydroxyapatite and reduces the number of products and lengthens of the process stone of consolidation required by the Ferroni-Dini method. It is possible that other calcium phosphate phases may be formed with our procedure and that they will be affected both by the Ca/P ratio (determined by the initial DAP concentration and by the amount of gypsum) and by the pH. With this in mind, we will also be analyzing the formation of other calcium phosphate phases.

For the reasons set out above, by treating the gypsum crust as a source of calcium we can eliminate the sulfate at the same time. In this way we can consolidate and clean the damaged stone, so achieving two objectives in a single application. In this cleaning and consolidation reaction, the resulting compounds fix the ammonium released hindering its use by microorganisms.

2. Materials and experimental procedure

2.1. Stone base material

The stone used was Arenisca Ronda (AR), a pinkish calcarenite quarried in Ronda (Malaga). This stone has quite a homogeneous mineralogical composition, granulometry and porosity. It is composed above all of calcite (>95%) and has an average grain size of between 1 and 2 mm, a porosity of 17%, a texture that varies between clast-supported and matrix-supported and finally a structure between massive and laminated slightly marked by the orientation of the clasts [23].

2.2. Selecting the best application method

In order to precipitate the CaPs via the reaction between the DAP and the gypsum, a total of 30 test samples measuring $2.5 \times 2 \times 1$ cm were submerged in a sulfuric acid solution with a concentration of 1 M for a period of two hours in order to induce the precipitation of gypsum. After 2 h, the samples were left to dry for 48 h in a BINDER KMF15 climate chamber under stable temperature and relative humidity conditions of 25 °C and 40% RH, respectively. Once the gypsum crust had been formed and in order to perform the cleaning and consolidation of the altered test samples at the same time, we used an ARBOCEL BC 300 cellulose pulp poultice to diffuse the DAP into the stone. In order to prevent the solution from evaporation, the samples and the poultices were wrapped together in a 5 μm thick laminated polyethylene protective film. Finally, in order to observe any possible differences resulting from different application times of the cellulose poultice, we used different samples in which the solution was applied for 10, 20, 30, 40, 50, 60, 90, 120, 180 and 240 min (hereafter along the results indicated as 10 m, 20 m, etc.).

2.3. Test methods

2.3.1. DAP concentrations

In order to discern the effects of the DAP concentration when it is applied in the form of a cellulose poultice on altered samples of Arenisca Ronda (AR), five tests were conducted in which a fixed amount of DAP (0.5, 1, 1.5, 2 and 3 M) were added to 100 mL of a saturated solution in gypsum allowing us to register the variations in the concentration of free Ca^{2+} , in the pH and in the transmittance

of the solutions. Tests were performed using a Titrand 905 system (Metrohm) controlled by a computer with the Tiamo v2.5 software. A continuous data log was also kept. The system was coupled to a pH-meter (Electrode Plus mod. 6.0262.100, Metrohm), a thermostatic bath (TC-602, Brookfield, USA), an ion-selective Ca^{2+} probe (DX240, Mettler Toledo) and a stirrer module (801 Stirrer, Metrohm).

2.3.2. Recording the evolution of the phosphate phases

In the case in which we applied a solution with a DAP concentration of 3 M, we used X-ray diffraction (XRD) to record the evolution of the phases formed by the reaction of the DAP with the gypsum crust in samples treated for different periods with a cellulose pulp poultice. The size of the samples was such that they could be coupled to the diffractometer camera for analysis without having to be cut. This enabled us to take the various measurements over time on the same surfaces. We used a Philips PW 1710 diffractometer equipped with an automatic slit. The working conditions were as follows: $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$), 40 kV voltage, a current of 40 mA, an explored area of 3° – 60° 2θ and a goniometer speed of $0.05 \text{ } 2\theta\text{s}^{-1}$. Goniometer calibration was performed using a silicon standard. The X Powder[®] [19] software and the JCPDS database were used for interpreting the data.

We also complement the surface analysis of the samples treated with DAP using a micro-Raman (μRM) Jasco NRS-5100 spectrometer, with an analyzed spectrum range of between 200 and 1250 cm^{-1} . Samples were studied after 24 h ($t = 1$ day), one week ($t = 7$ days) and one month ($t = 30$ days) after application of the DAP solution.

2.3.3. Characterization of the visual appearance of the stone and microtextural changes

The visual appearance of the stone is fundamental as it is one of its most easily observable intrinsic properties. We began by recording the values for the healthy samples so as later to be able to compare any differences that may have been caused by the gypsum crust or the treatment with DAP at different poultice application times. For this experiment we used a Minolta CM-700D spectrophotometer equipped with a xenon lamp and diffuse reflectance geometry. We followed the UNE-EN 15886 [45] standard and the measurement conditions were as follows: illumination diameter of 8 mm, specular component in SCI mode (this mode measures both light reflected specularly and light reflected diffusely), wavelength range from 360 to 740 nm with an interval of 10 nm and the illuminant mode used in the taking of measurements was $10^\circ/\text{D65}$. The difference in color (ΔE^*) was calculated using the following equation (EN 15886, 2011):

$$\Delta E^* = ((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2)^{1/2} \quad (3)$$

where L^* is the lightness and a^* and b^* the chromatic parameters. The chromaticity (C^*) was also calculated. In order to characterize the changes that have taken place on the surface of the test samples, we measured their roughness immediately after removing the poultice ($t = 0$ days) and a month later before ($t = 30$ days) and after ($t = 30$ days – washed) washing the samples. For this purpose we used a Leica video-microscope model DVM2000 (DVM) with a 50–400x lens (and a corrective lens of 0.4x). The data and images were processed using the Leica Application Suite v3.8.0 (Leica Microsystems[®]) and Leica Maps Start v6.2.7200 (Digital Surf[®]) software.

The changes at microtextural level were analyzed in greater detail a month after application of the consolidant using a Hitachi S-510 scanning electronic microscope (SEM) in BSE mode and equipped with an EDX microanalysis system. The samples were

not metalized so as to enable us to conduct different tests on the same samples over time, so minimizing interruption of the consolidation process.

2.3.4. Efficacy of the treatment

In order to evaluate the efficacy of the consolidation treatment and of the penetrability of the DAP, we measured the resistance to drilling (in N) by using a Drilling Resistance Measuring System (DRMS) Cordless drill with a flat-edged 5 mm diameter bit with a diamond-covered tip (Sint Technology). The working conditions were as follows: rotational speed, $\omega = 600 \text{ rpm}$; penetration rate, $v = 10 \text{ mm/min}$ and penetration depth of 4 mm. The drilling measurements were controlled using a calibration standard (ARS, Sint Technology). The results of the drilling were standardized to the diameter of the bit, and the values were presented in N mm^{-1} [30].

2.3.5. Evolution over time of the consolidant treatment

Once the tests described above had been performed, we washed the surface of the samples with distilled water (samples identified as “w or washed”) in order to eliminate the ammonium sulfate and any excess of unreacted DAP that might still remain. We then analyzed them again using XRD, μRS , DVM and spectrophotometer in order to assess the degree of efficacy of this method in terms of the elimination of gypsum. We carried out the same experiments again six months after application of the consolidant on the washed samples ($t = 180$ days-w/-washed), so as to gain a more complete picture of the evolution over time of the consolidant treatment.

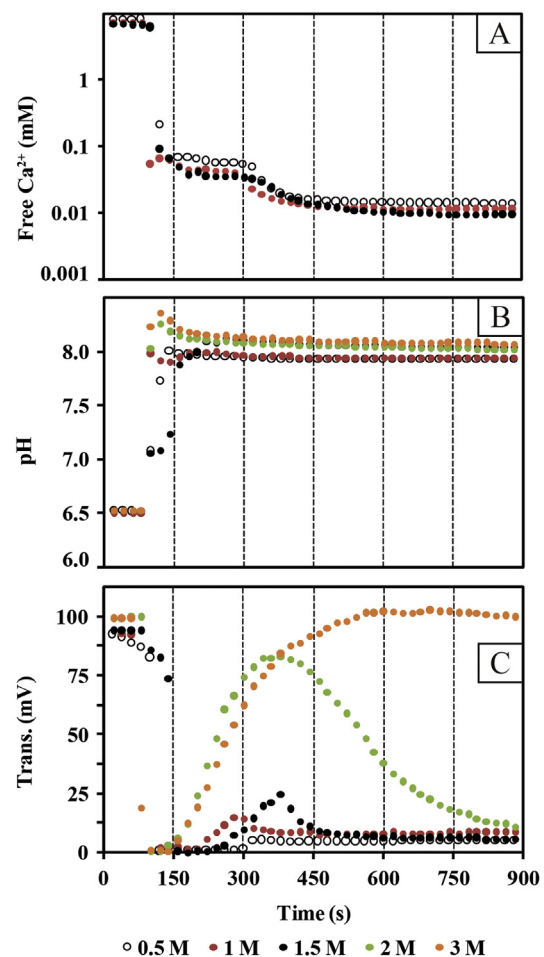


Fig. 1. Graphs showing the variations in free calcium (A), pH (B) and turbidity (C) of the gypsum-saturated solutions due to the addition of DAP at concentrations of 0.5, 1, 1.5, 2 and 3 M.

3. Results and discussions

3.1. Gypsum-DAP dissolutions

The values for free calcium (A), pH (B) and transmittance (C) of the solutions saturated in gypsum and at different concentrations of DAP are shown in Fig. 1. As regards the variation in free calcium in solution (Fig. 1A), we were only able to present the results for the 0.5, 1 and 1.5 M DAP concentrations given that for concentrations in excess of 1.5 M the calcium values became less linear and more unrepresentative. The process for assimilating the free calcium takes place in two clearly differentiated stages, of which the first is more important due to the addition of the DAP to the solution. We also observed that the amount of free calcium in the solution falls as the amount of DAP added increases, although the difference between the three concentrations seems minimal. In addition to these two stages (recorded at approximately 100–120 and 300–320 s) may be due to the precipitation of the two phases of amorphous calcium phosphate (ACP1 and ACP2) described by Christoffersen et al. [6], Christoffersen et al. [7], which could give rise to other CaPs. Indeed a much higher amount of calcium is fixed in the first jump on the graph than in the second. This means that the phosphate phases that develop in these two stages may be different. Fig. 1B shows the pH values and an increase in this parameter can be clearly seen when the DAP is added to the solution. Shortly afterwards, the pH value falls slightly before stabilizing until the end of the test in all cases. At low concentrations (0.5 and 1 M) of DAP the pH stabilizes at around 8, while from 1.5 M it stabilizes at slightly higher values, although the difference is small. This slight difference in pH could affect the level of precipitation, when the consolidant is applied with a poultice, ultimately affecting the CaPs, given that pH can have a strong influence on precipitation [4,41,22]. As regards the transmittance of the solution (Fig. 1C) we observed that the time required for the mineral phases to precipitate increased in line with the concentration of DAP. This means that adding NH_4^+ and PO_4^{2-} to water increases water viscosity, which becomes important for the 3 M DAP solution. In fact the influence of pH on the precipitation of CaPs in oversaturated solution was demonstrated in research by Song et al. [42]. We even observed that at a pH of around 8 and depending on the reaction time, the precipitation of the phases was accelerated. For all these reasons, we concluded that viscosity plays a crucial role in the precipitation of the different CaPs together with pH.

In spite of these results, the decision to apply a DAP 3 M solution to the altered samples was based on the following criteria: (a) a high oversaturation of DAP will ensure a total reaction with the gypsum; (b) the slowing down of the precipitation of the CaPs observed in the solutions could be used to enhance the penetrability of the treatment, prevent the formation of very superficial crusts and prevent atmospheric pollutants from acting at depth; (c) establish whether the 3 M solution is sufficient to ensure that good results are obtained with this treatment or whether higher concentrations are required.

3.2. Evolution of the calcium phosphate as a result of the reaction with gypsum

The results of the XRD analysis are shown in Figs. 2–4. Fig. 2 shows the evolution of the consolidation process using DAP at 3 M in accordance with the initial hypothesis, i.e. the precipitation of the calcium phosphate phases can be enhanced by eliminating the gypsum from the crust on the stone. The noise in the diffractograms increases in line with the poultice application time (from 10 m to 240 m) and this same noise falls over time post-application (from 0 days to 30 days). The reduction in the noise over time is

due to the appearance of calcium phosphate phases, which are initially amorphous and gradually evolve towards more crystalline phases [9]. In addition, as the phosphate phases appear, the reflections of the gypsum become less intense with regard to application time, and that at 120 m there is no record of this phase, even immediately after the poultice with the DAP solution is removed ($t = 0$ days). This behavior was to be expected and suggests that the longer the application time the higher the amounts of DAP and gypsum that react. In addition and with the exception of the 10 m sample, gypsum was not detected 24 h after the application of the treatment ($t = 1$ day), which means that the reaction in which gypsum is replaced by calcium phosphate continues even after the poultice has been removed. In addition in very short application periods of only 20 min, the gypsum appears to be entirely eliminated from the surface. Finally the differences we observed between the samples after one day ($t = 1$ day) and one week ($t = 7$ days) are more pronounced than between one week and one month ($t = 30$ days), which indicates that the greatest mineralogical transformations take place in the space of one week. This means that a short application time is required which together with the rapid replacement of the gypsum by CaPs are two positive factors to be taken into account when considering applying this method in consolidation work.

Given that there was no difference between the samples in terms of application times or in the development of the different phases of CaPs, we selected the 30 m, 60 m and 240 m samples as representative of the whole set of samples so as to establish: (a) the minimum time required for the consolidant to do its job at the selected concentration; (b) the amount of gypsum eliminated; (c) the quality of the film of consolidant formed on the surface of the stone and (d) the penetrability of the consolidant. Fig. 3 shows the XRD results for the samples treated for 30, 60 and 240 min (Fig. 3A–C, respectively). In general, when the poultice is removed ($t = 0$) amorphous phases of ACP appear to be present due to the significant amount of background noise in the diffractograms. As time goes by there is an increase in the quantity and crystallinity of the different CaPs and of ammonium sulfate (NH-S). If we compare the three application time intervals, the best results were obtained at 60 m, due in part to greater development of CaPs (OCP, TCP, HAP and DCPD) and in particular to the fact that at the end of the treatment gypsum could not be identified which implies that it had been completely eliminated. This means that the treatment is most effective at an application time of 60 min. Another sign that the treatment is working correctly is when ammonium sulfate (NH-S) begins to form a few hours after application; a progressive increase in the amount of NH-S is also observed as the reaction period increases. By contrast the amount of DAP falls with time due to the reaction with the gypsum. Nonetheless the relative amount of DAP remaining falls as the poultice application time increases. In other words at the same number of days after removal of the poultice, there was less DAP remaining in the 240 m sample than in the 60 m sample, which itself had less DAP than the 30 m sample. After washing the samples the NH-S phase completely disappeared, so confirming how easy it is to eliminate the sub-products of the method (ammonium and sulfate ions). The reaction with the DAP eliminated the gypsum entirely in the 60 m sample, although this did not happen in the 30 m sample and above all in the 240 m sample. Whereas in the 30 m sample, the presence of gypsum may be due to insufficient application time, in the 240 m sample the long application period may have complicated the diffusion of the DAP, especially due to the slowing down of the process due to the viscosity of the solution. The water saturation of the may also have played an important role in this process, acting in a negative way at long application times. Finally we should point out that after washing the samples and leaving them to dry, we observed a slight increase

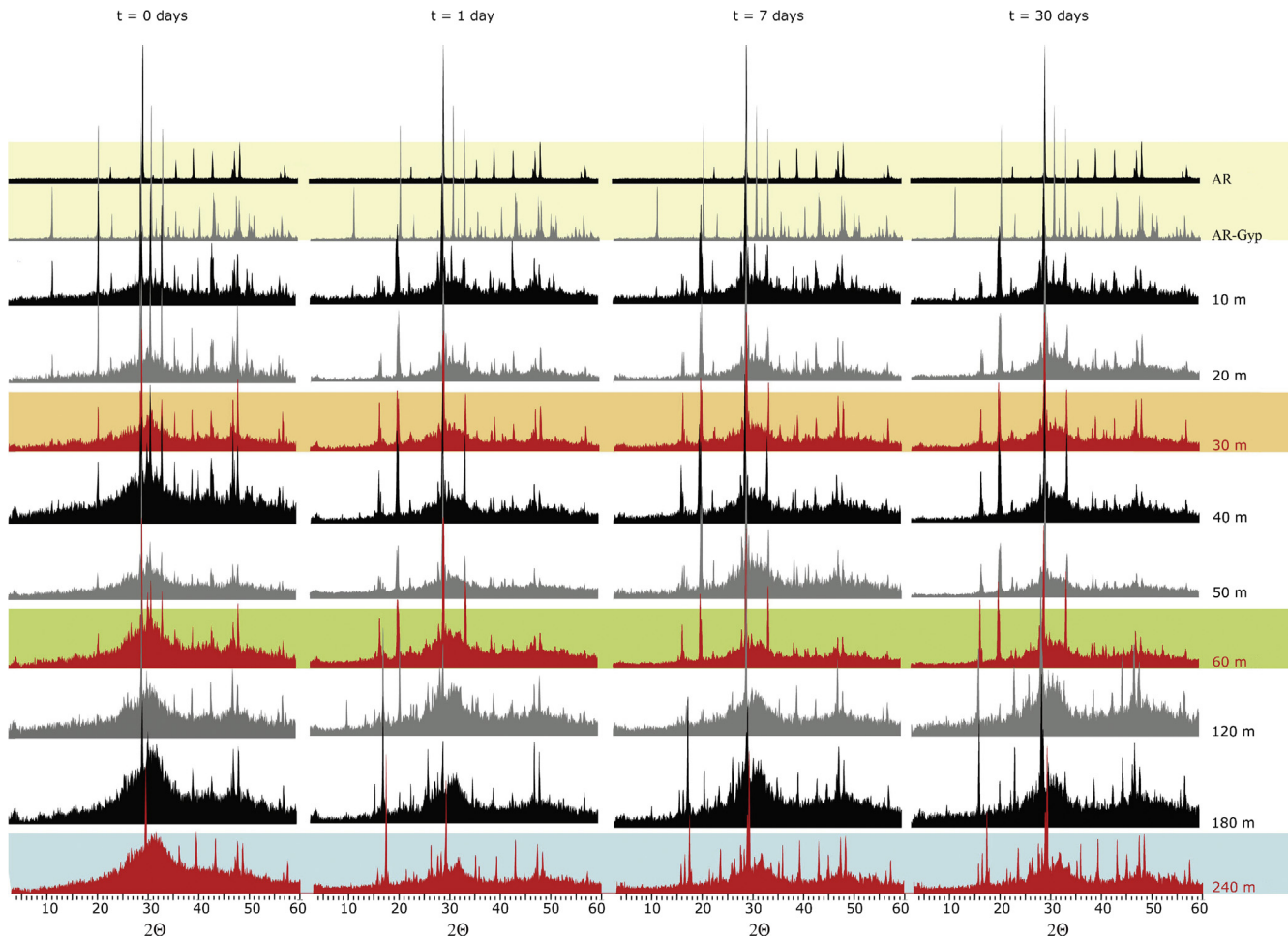


Fig. 2. Evolution of the consolidant assessed using XRD over the first 30 days after application of DAP using a poultice at different application times (10 m, 20 m, 30 m, 40 m, 50 m, 60 m, 120 m, 180 m and 240 m) and compared to the healthy sample (AR) and the altered sample with the gypsum crust (AR-Gyp).

in the noise and an increase in the amount of DAP in the 30(w) and 180(w) diffractograms. It is possible that a small amount of DAP in the deepest parts of the consolidant film does not react and is brought to the surface when the sample is washed. It is also possible that this excess DAP may again give rise to the precipitation of CaPs as the results seem to indicate.

We also compared the mineralogical evolution of the samples treated at 3 M with those treated with solutions of 1 and 2 M DAP, for which purpose we conducted XRD analysis of the samples treated with application times of 30 and 60 min (30 m and 60 m samples). The 240 m sample was excluded because of the problems it has shown in terms of its capacity for removing the gypsum. The results show that at 30 days the reactions had already finished (Fig. 4). The formation of brushite is greater the lower the initial concentration of DAP and regardless of the application time, while the amount of excess DAP increases in line with the initially applied concentration. This means that a low saturation of the initial solution favors the precipitation of this phase compared to others with a higher Ca/P ratio [41]. The presence of gypsum was detected in the samples treated at 1 M, which means that treatment at this concentration is not as effective in either the 30 m or 60 m samples. After washing the samples, the amount of unreacted gypsum remaining falls as the initial concentration of DAP increases. Finally we observed that the initial concentration of DAP determines what CaP phase precipitates, observing in general that higher concentrations of DAP enhance the precipitation of phases with a higher Ca/P ratio; however a lower amount of these

phases was recorded when a concentration of DAP 3 M was used than when 1 and 2 M were used, in which there was a strong presence of brushite compared with 3 M and compared with the other phases. It is possible that at high DAP concentrations (and therefore probably at higher initial oversaturation with respect to the CaPs), the precursor phases of the HAP, and the HAP itself show low crystallinity as suggested by the higher levels of noise registered at 3 M, which results in lower intensity of the reflections.

In order to complete the mineralogical study we identified the phases present in the 30 m, 60 m and 240 m samples using μ RM (Fig. 5). We based our interpretation of these results on the data provided by Sassoni et al. [39]. The results show similarities with those obtained using XRD so confirming the presence of different phases of CaPs or the reduction in noise over time as the consolidant matures; although we had some difficulties in assigning the bands, as not all the bands associated with each phase appeared. Greater differences compared to the XRD analysis can be seen after washing the samples. The tricalcium phosphate (TCP) disappears and a new phase identified as monocalcium phosphate monohydrate (MCPM) appears. In other words a new phase is precipitated that is poorer in calcium due to the washing of the samples and to the fact that most of the available calcium has already been fixed by other CaPs. This transformation could also be favored by the fact that the TCP has small vacancies in which it is difficult to accommodate calcium ions. As a result these vacancies are normally filled by magnesium ions [15]. However this process occurs above all in the 30 m and 60 m samples, which, as we have seen earlier,

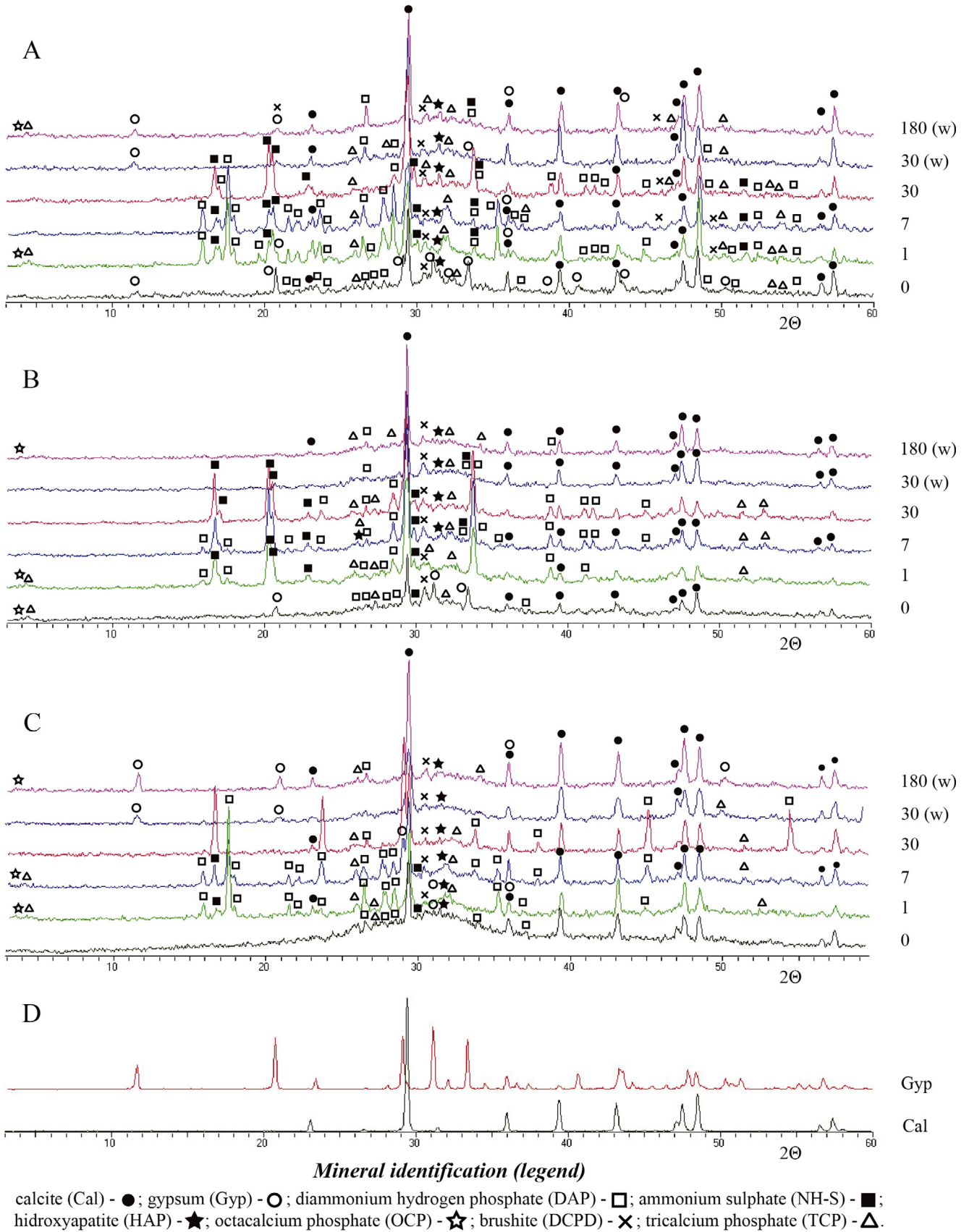


Fig. 3. Evolution of the consolidant (DAP 3 M) assessed using XRD in the 30 m (A), 60 m (B) and 240 m (C) samples and the standards for gypsum and calcite (Gyp and Cal, D). The measurements were taken immediately after removing the poultice (0), one day later (1), one week later (7), one month later before and after washing the samples (30 and 30 (w), respectively) and six months later (180 (w)). The following mineral identification cards were used: calcite “5-586”, gypsum “21-816”, phosphammite (dibasic ammonium phosphate) “29-111”, hydroxylapatite “9-432”, tricalcium phosphate (V) and whitlockite “86-1585 and 9-169, respectively”, calcium hydrogen phosphate hydrate and calcium hydrogen phosphate (octacalcium phosphate “26-1056 and 79-423, respectively”, brushite “4-740” and ammonium sulphate “1-343”.

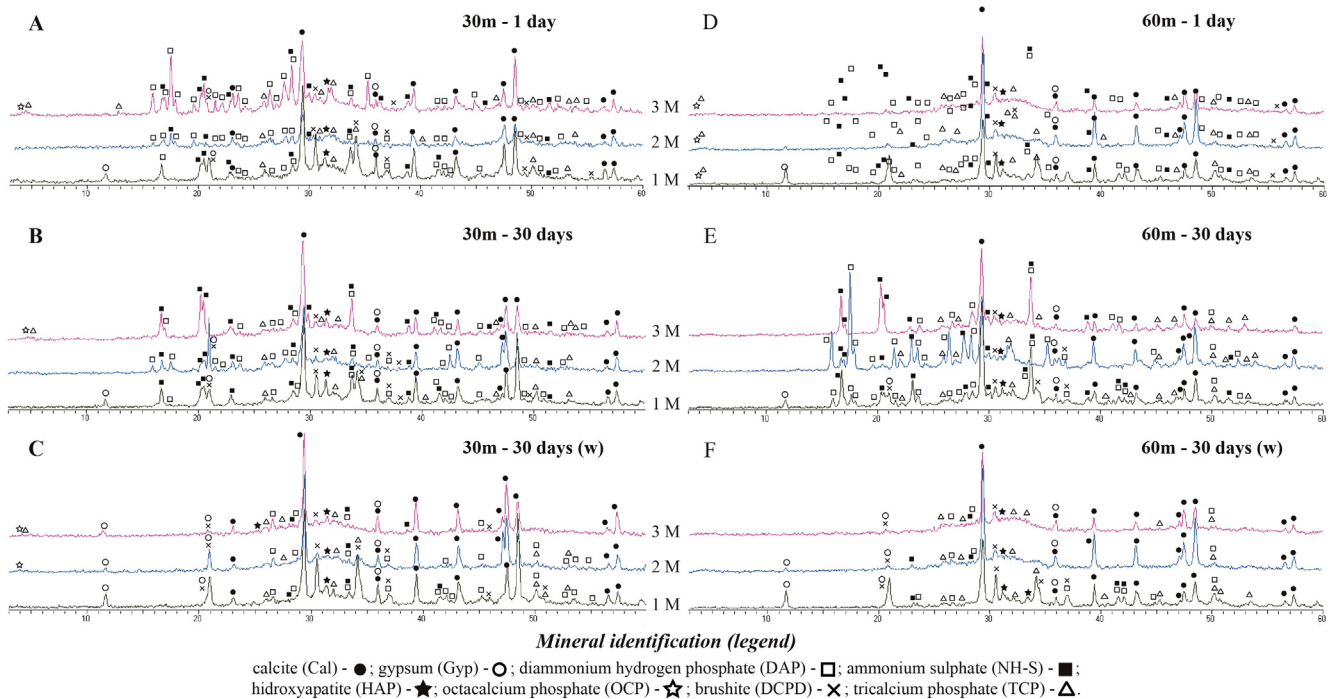


Fig. 4. Comparative diagram for the 30 m (A, B and C) y 60 m (D, E and F) samples treated at concentrations of 1 M, 2 M and 3 M after one day (A and B) and 30 days before (Band E) and after (C and F) washing.

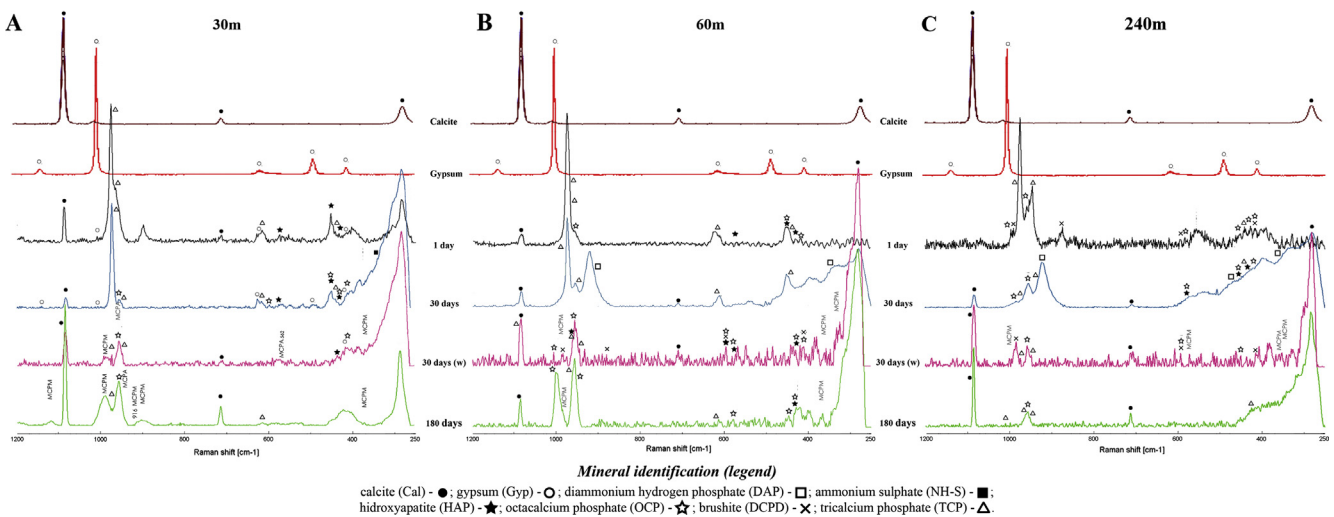


Fig. 5. Raman spectra of the calcite and gypsum standards (RRUFF) of the 30 m, 60 m and 240 m samples (A, B and C, respectively) after one day (1 day), one month before (30 days) and after (30 days (w)) washing and finally after six months (180 days). The mineral legend is indicated in the figure.

behaved differently from the 240 m sample. Indeed in this last sample, the TCP has not disappeared completely and there is a smaller amount of MCPM. On the other hand, after six months there is practically no MCPM, which suggests that it has been transformed into other phases.

The evolution of the mineral phases can be explained by the Gay-Lussac-Ostwald or Ostwald step rule. Thus, the stone-gypsum-DAP system preferentially forms the phase with the fastest precipitation rate under the prevailing conditions. The nucleation of a more soluble phase (such as amorphous or brushite) is kinetically favored over other less soluble analogues (such as HAP) because of the lower interfacial energy (and thus lower nucleation energy) between minerals and solution. Hence, when the oversaturation of the solution is sufficiently high, the meta-

stable mineral may have a higher rate of precipitation. In other words, the solid that reduces oversaturation quickest will form first. In order to verify this fact, Fig. 6 shows the evolution of the saturation indices (SI) for the different phases that precipitate during the interaction of the gypsum with the 1 M solution of DAP. Calculations were made with PHREEQC program using the Minteq v4 database, which was used in previous similar research [3,17]. We did not perform calculations for the selected concentration (3 M) because the ion-association aqueous model does not run for high values of solution ionic strength. In the papers referred to above there was a discrepancy in the equilibrium constant values (pK) and we therefore decided to use the pKs indicated in Table 1. As the amorphous phase has a variable amount of water, we took two amorphous phases to make the calculations, one with

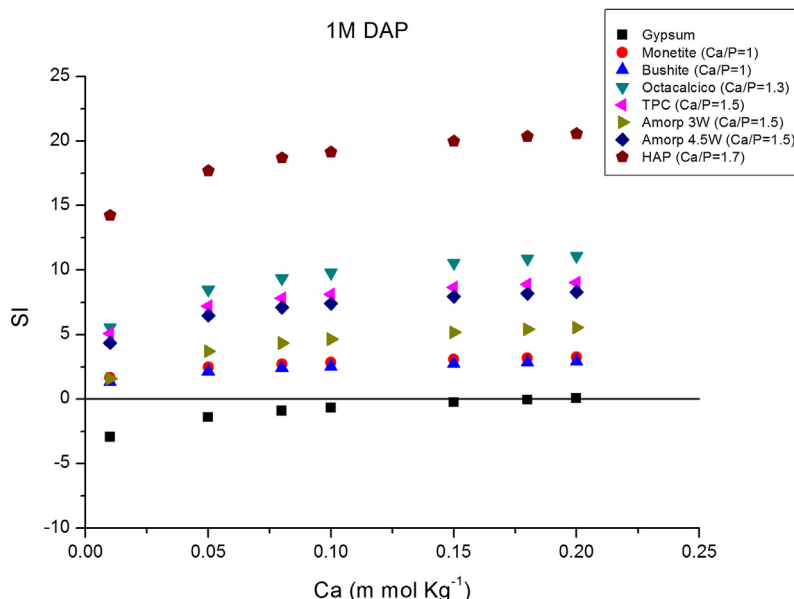


Fig. 6. Saturation index (SI) values for the different calcium phosphate phases calculated using Phreeqc (Minteq v4 database) for a stone-plaster-DAP (1 M) system.

Table 1

Values of the pKs used and formulae of the different phases involved in the reaction.

Solid phases	Formulae	pKs	References
Gypsum	CaSO ₄ ·2H ₂ O	4.61	Minteq v4
ACP_3	Ca ₃ (PO ₄) ₂ ·3H ₂ O	25.50	[9]
ACP_4.5	Ca ₃ (PO ₄) ₂ ·4.5H ₂ O	28.30	[9]
MCPD	CaHPO ₄	19.27	Minteq v4; Barat et al. [3]
DCPD	CaHPO ₄ ·2H ₂ O	19.00	Minteq v4; Barat et al. [3]
TCP	Ca ₃ (PO ₄) ₂ (beta)	28.92	Minteq v4; Barat et al. [3]
OCP	Ca ₄ H(PO ₄) ₃ ·3H ₂ O	47.08	Minteq v4; Barat et al. [3]
HAP	Ca ₅ (PO ₄) ₃ OH	44.33	Minteq v4; Barat et al. [3]

3 and the other with 4.5 water molecules (ACP_3 and ACP_4, respectively). In the same figure we can see that the ACP and (MCPM) DCPD phases are more soluble and would therefore be formed first, according to the Ostwald step rule [12]. However due to the behavior observed in the solutions prepared at different concentrations, the oversaturation of the initial solution (3 M) and of the pH would first cause the precipitation of CaPs with a higher Ca/P ratio and later precipitate phases with a lower saturation index [41]. In particular, Mekmene et al. [22] observed that the initial pH had a direct influence on the presence or absence of brushite, given that when the initial pH was kept constant, brushite was not observed although calcium-deficient hydroxyapatite was. Finally Van Kemenade and De Bruyn [47] found that in the 7.4–8.5 pH range the ACP phase evolved to OCP. This means that in addition to the influence of pH described earlier, this initial variation in pH together with the final value could favor the precipitation of all the recorded phases –DCPD, OCP, TCP and HAP– and the low crystallinity of the phases with a high Ca/P ratio.

3.3. Chromatic and surface aspects

Fig. 7 shows the values for lightness (L^*) (Fig. 7A), chromaticity (C^*) (Fig. 7B) and color difference (ΔE^* , Fig. 7C) for the sample with the gypsum crust (Gyp) and the samples treated with a 3 M solution at different times (from 10 m to 240 m), as compared to the healthy sample and finally the color difference between the treated samples and the sample with the gypsum crust (ΔE^* , Fig. 7D). If we want to apply this treatment in real buildings, assessing the color is

essential to verify whether or not the treatment causes perceptible visual changes in the stone. The first change we observed was, as might be expected, that the gypsum crust has produced an increase in lightness and a reduction in chromaticity. In general, the treated samples did not recover the original values of the healthy sample and in most cases color difference increased. As regards the three standard samples (30 m, 60 m and 240 m), the 30 m sample showed the greatest difference from the healthy sample, with a significant increase in lightness and a fall in chromaticity. This change was more evident after the excess DAP and NH-S had been washed off. The continuous evolution of the film of consolidant after 180 days made the differences even more evident. The best results were achieved by the 240 m sample in that the L^* and C^* values of the washed samples at both 30 and 180 days tended to recover those of the healthy sample reaching the values of the altered sample with the gypsum crust. Finally, the color difference ΔE^* between the treated samples and the samples with the gypsum crust (Fig. 7D), was almost always less than three units, which means that the change cannot be detected by the naked eye [14]. This means that although the treatment did not return the values to those of the healthy stone, it did not cause a greater visual change than that caused by the gypsum crust.

Observation of the treated samples using DVM (Fig. 8) revealed the following: (1) the surface of the 60 m sample is less rough than that of the 30 m and 240 m samples, the latter of which is favored by the evolution of the consolidant film over time; (2) a very fine film that is rich in NH-S (and excess DAP) can be clearly distinguished as these areas have a greyer tone than the rest of the surface (indicated with red arrows); (3) when the samples are washed the areas rich in NH-S and DAP are eliminated; (4) after washing, the fissuring of the CaP film is a little more evident in the 30 m sample and slightly more so in the 60 m; in the 240 m sample however the fissuring process has been so intense that fragments of the consolidant film have fallen off. Clearly, the presence of fissures represent a drawback, especially in 240 m sample, since a good consolidant must be completely adhered to the substrate; (5) no visual differences were observed between the washed samples after 30 days and 180 days or in terms of roughness.

On the basis of the DVM results, we deduced that changes in the color of the samples are associated with changes in the roughness of the surface and the loss of fragments of the film. For example in

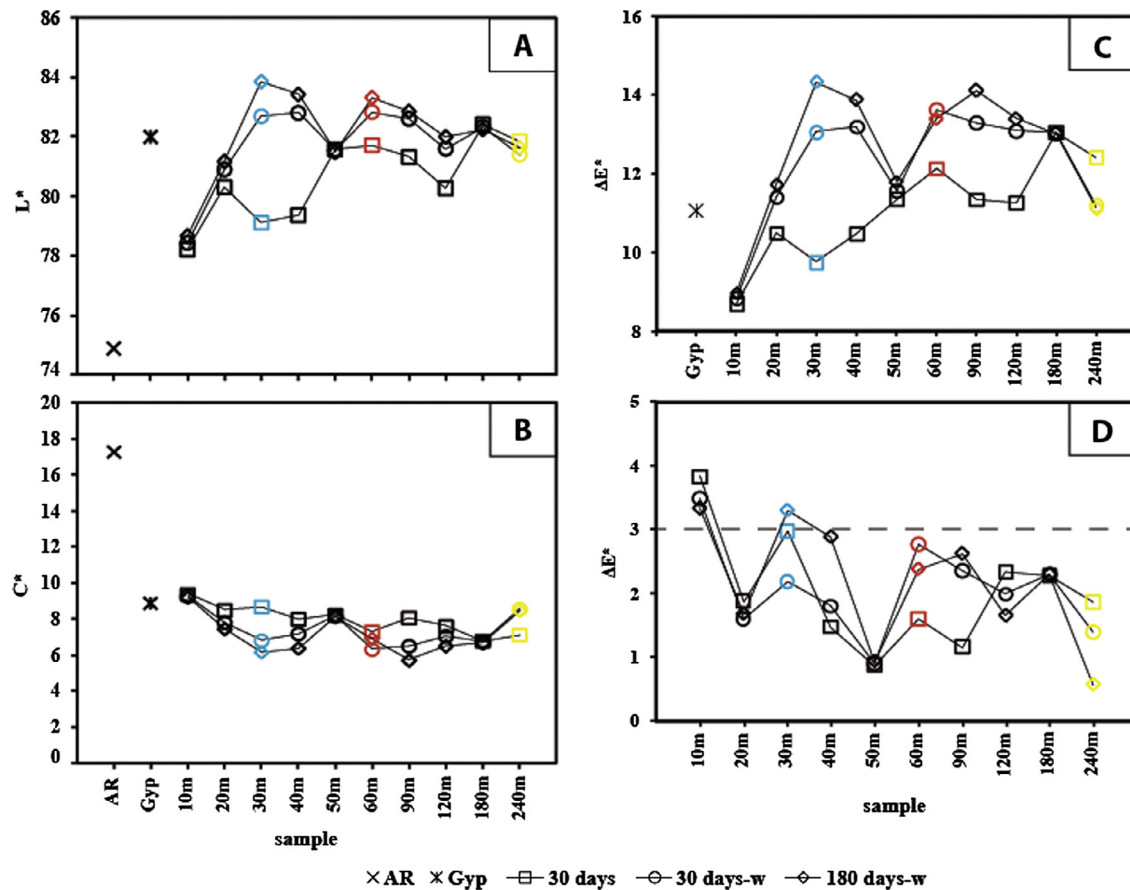


Fig. 7. Values for the chromatic parameters A: lightness (L^*); B: chromaticity (C^*); C: color difference (ΔE^*) of the altered sample with the gypsum crust and those treated at the different times compared to the healthy stone; D: color difference (ΔE^*) between the treated samples and the altered sample with the gypsum crust. The values are obtained after 30 days, before and after the samples were washed (square and circle symbols respectively) and after 180 days (rhombus symbol). The discontinuous line indicates the $\Delta E^* = 3$ value, the limit for color changes perceptible to the eye.

the case of the 30 m sample, the homogeneity observed in the film led to an increase in lightness (L^*). In the 240 m sample by contrast, the disappearance of parts of the film caused the surface of the original stone to reappear, which means that the color values are similar to those of the healthy sample. This means that our assertion that the 240 m application appears to be the best for recovering the original color of the material is largely but due to the fact that fragments of the film of consolidant fall off, so revealing the original stone.

3.4. Textural evolution

Fig. 9 shows the ESEM microphotographs of the altered stone samples with a gypsum crust (A-a), those treated with DAP 3 M after 30 days before being washed (B-b, C-c and D-d) and after being washed and after 180 days had elapsed (E-e, F-f and G-g). In this case we also used the 30 m, 60 m and 240 m samples, and we also included an overhead image (lower case letters) of the surface and one of the profile (upper case letters), in which we can observe the sequence from the upper surface (crust of consolidant) to the core (carbonate matrix) of the sample. The gypsum crust has been deposited on the surface of the samples (Fig. 9A), in some cases reaching a thickness of 30 μm and penetrating to a maximum depth of 60–80 μm . This crust appears in general to have a massive form with an acicular-radial habit (Fig. 9a) with an average crystal size of about 20–30 μm . In the samples tested before being washed, we observed that the consolidant has produced a stratification that is practically identical in all three samples (Fig. 9B–D). In this

stratification, two strata called 1 and 2 can be clearly distinguished. Working from the upper surface, stratum 1 is a crust composed fundamentally of CaPs with a very small quantity of gypsum, whereas stratum 2 has a massive compact appearance and is composed exclusively of CaPs. It varies in thickness from 150 to 350 μm , a value which increases in line with the poultice application time. A fissure appears between stratum 2 and the healthy stone which varies in width from a few micrometers up to 30–35 μm . The reason for this fissure is not clear but there are two factors that may have caused it to appear which are not mutually exclusive. The first factor may be linked to the earlier decay caused by the acid attack and the formation of the gypsum crust and the second factor is the predisposition of this stone when it starts to decay to fissures with the same orientation as the clasts [23]. The observations made on the surface of the samples (Fig. 9b–d) have enabled us to identify four different habits in the CaPs crystals. The columnar habit appeared above all in the 30 m sample (Fig. 9b); the acicular habit in aggregates is characteristic of the 60 m sample (Fig. 9c); the massive habit was very common in the 240 m sample (Fig. 9-d); and finally the flake-type habit appeared in all three samples. By direct observation of the samples we can deduce that the columnar and the flake-type habits are due to direct precipitation from the solution when it takes up the free calcium cations in the solution, while the acicular habit occurs by replacement of the gypsum aggregates. In any case, the habits we observed were characteristic features of each sample but were not exclusive. ESEM observation confirms that the 240 m sample has the most fissures.

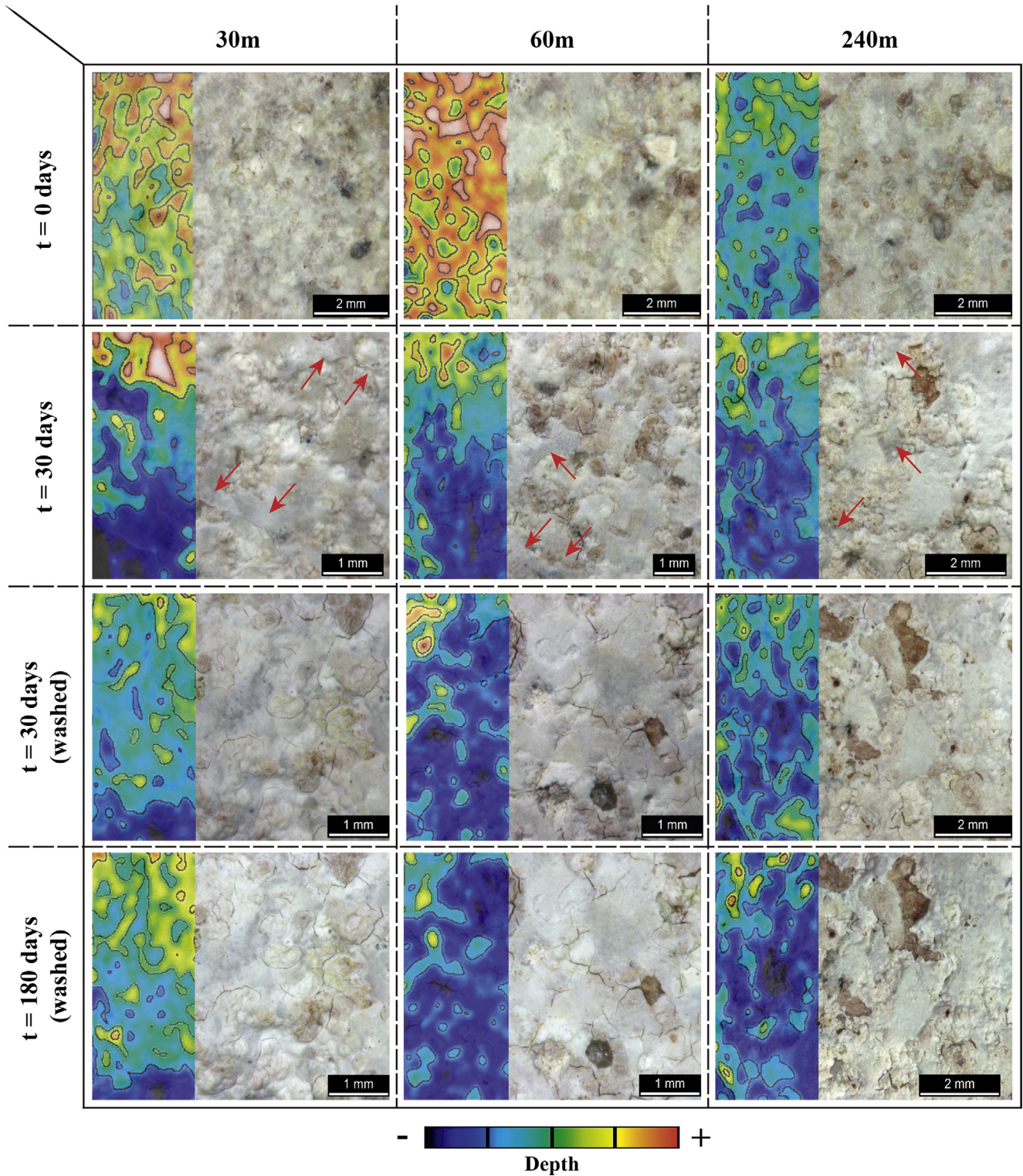


Fig. 8. Images of the surface and the roughness obtained using VDM of the 30 m, 60 m and 240 m samples when the poultice with DAP was removed ($t = 0$ days), after a month before ($t = 30$ days) and after ($t = 30$ days (washed)) washing and finally after six months ($t = 180$ days (washed)). The color scale indicates in relative values the homogeneity of the roughness registered on the surface.

The washed samples analyzed after six months of treatment with the consolidant (Fig. 9E-e, F-f and G-g) show a textural evolution of the consolidant. At 30 days, the stratification of the consolidant on the stone can still be observed although the separation between strata 1 and 2 is not as clear as in previous cases. Fissures can still be observed between the consolidant and the substrate.

We also observed that new CaP crystals with a mainly flake habit had formed on the substrate. Once again this type of habit confirms that the crystals result from the direct precipitation of the solution, regardless of the type of the substrate. CaP crystals generally appear in massive form a fact more evident in the 30 m and 60 m samples (Fig. 9e and f, respectively) than in the 240 m sample

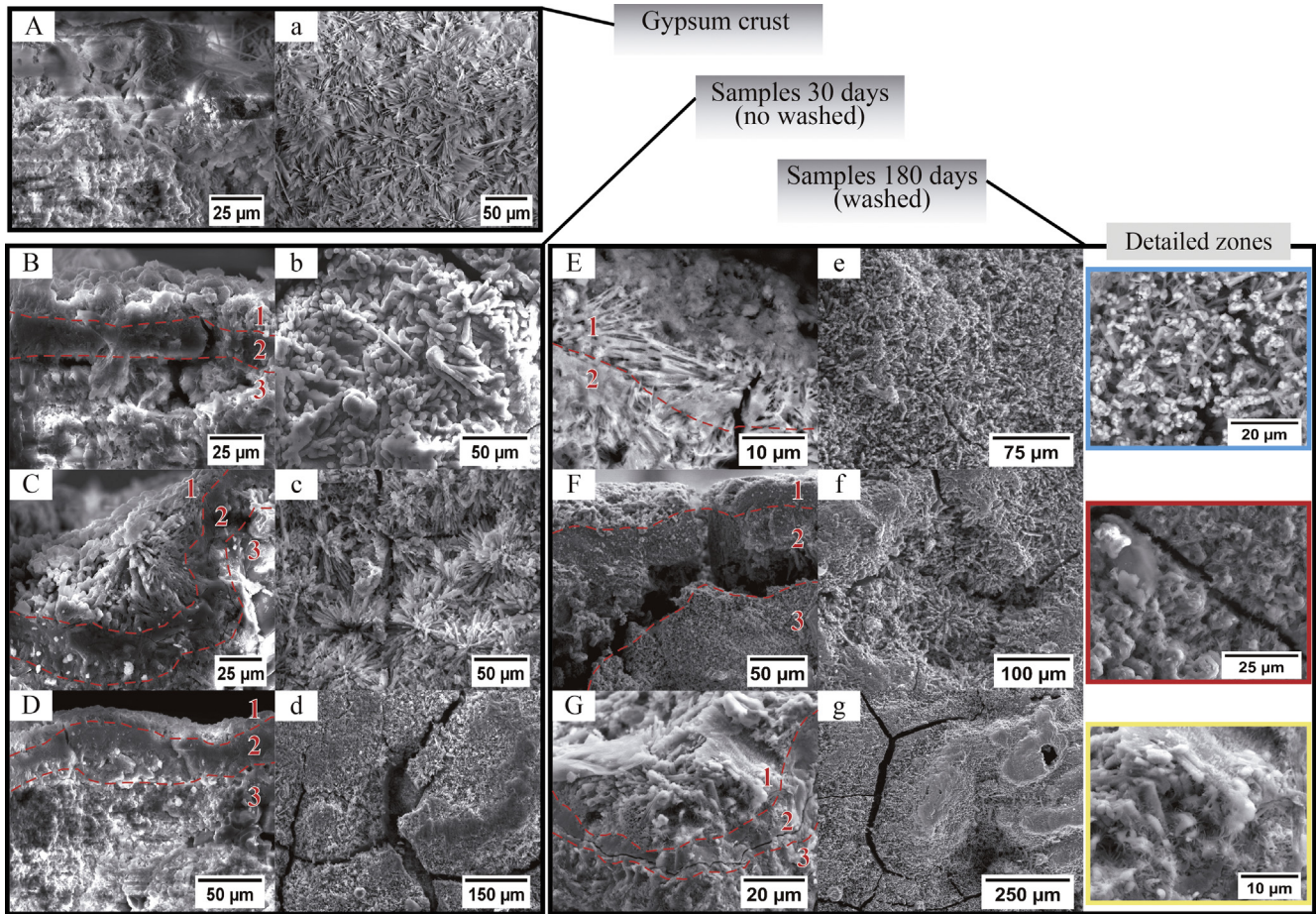
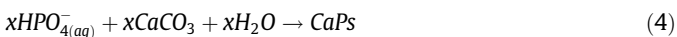


Fig. 9. ESEM microphotographs of the profile (uppercase letters) and of the surface (lowercase letters) of the gypsum crust (A-a), of the samples treated after 30 days, before being washed (B-b, C-c and D-d) and after being washed after 180 days of treatment (E-e, F-f and G-g). The images are of the 30 m (B-b and E-e), 60 m (C-c and F-f) and 240 m (D-d and G-g) samples. Legend: 1, replacement crust; 2, massive level of CaPs; 3, carbonate substrate.

(Fig. 9g). The degree of fissuring has remained constant. However we observed the precipitation of new smaller CaP crystals with acicular and flake habits in the fissures and on top of the stone substrate. We also observed botryoidal aggregates which could be amorphous phases or phases with low crystallinity. These may be related with the increase in noise detected by XRD in the samples after washing and would corroborate the presence of unreacted DAP beneath the film or even between the CaP crystals that developed at the beginning. This process highlights another advantage of this product and of the application method namely that it continues reacting and evolving over time. In fact from Eq. (2) described above, we deduced that if we start with a high initial amount of DAP, it is possible to generate an excess amount of hydrogen phosphate ions (HPO_4^{2-}) in solution. This excess amount of ions could react later with the calcite from the substrate (Eq. (4)) so giving rise to additional precipitation of calcium phosphates.



This reaction would of course depend on the initial concentration of DAP and of gypsum, which is more soluble than calcite. We should also mention that this excess DAP can be easily eliminated at the same time as the ammonium sulfate is removed and would therefore not create any additional problems.

3.5. Degree of consolidation

The resistance to microdrilling results is shown in Fig. 10. The average value of the healthy sample (black line, AR) is 1.27 N mm^{-1} . The R_d value for the altered sample with the gypsum crust (grey line, Gyp) is different from the healthy sample. In the figure we can see that the gypsum crust itself causes a substantial increase in resistance in a very superficial layer approximately $300 \mu\text{m}$ thick. Later at a depth of about 1 mm, this value falls below the average value for the healthy stone. This decline is evident down to approximately 4 mm from which point onwards the samples recover the values achieved by healthy stone. This shows that the accumulation of gypsum occurs above all in the first millimeter from the surface while between 1 and 4 mm there is a notable deterioration in the texture of the samples due to the acid attack. As regards the effectiveness of the treatment using CaPs, in general the results we obtained were positive, above all due to the fact that the consolidated samples (30 m, 60 m and 240 m) tend to have higher resistance than the healthy (AR) and altered (Gyp) samples. We can observe that the behavior of the treatment is very similar but presents little differences due to the application times and we also deduced that the penetration depth of this consolidant in the three cases studied was about 3.5–4 mm, below which point the values returned to those of healthy stone. Two aspects of the penetration and action of this consolidant are worth highlighting. The first is that the penetration depth coincides approximately with

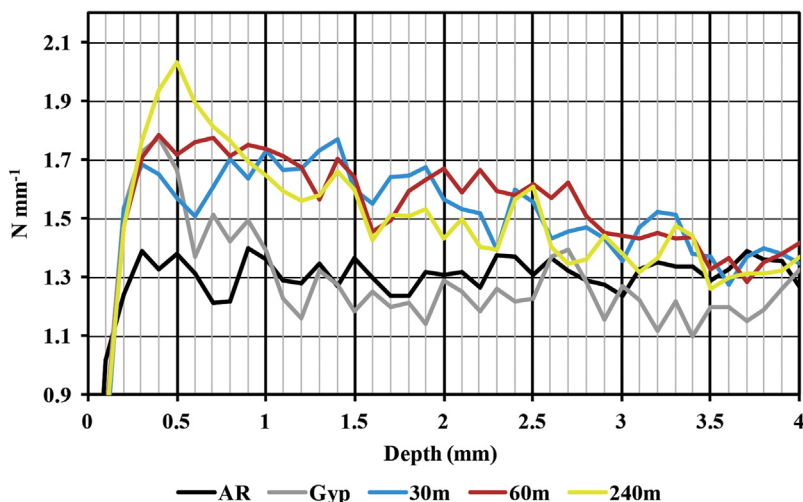


Fig. 10. Average values for resistance to microdrilling (R_p , in N/mm) of the healthy sample (AR), the altered sample with the gypsum crust (Gyp) and the samples treated for 30, 60 and 240 min (30 m, 60 m and 240 m, respectively).

the depth of the deterioration caused by the acid attack, which indicates that the damaged texture itself facilitates penetration and precipitation of the consolidant by reaction with the gypsum on the surface and the calcite below. The second point of interest is that this increase in resistance at increasing depth is linked to the degree of saturation of the solution, as the oversaturation of the treatment allowed penetration to this depth. In addition if we look at the different behavior of the 30 m, 60 m and 240 m samples (blue, red and yellow lines respectively), we can come to the following conclusions: (1) application time is important in the first millimeter of thickness from the surface in that it produces a significant increase in resistance due to the formation of the film of consolidant; (2) the 30 m and 60 m samples have similar results with an average R_d value of 1.48 and 1.51 N/mm , respectively; (3) although the 240 m sample has a higher resistance to drilling value in the first millimeter it later falls below that for the 30 m and 60 m samples ($R_d = 1.46 N/mm$).

These results demonstrate the effectiveness of the treatment, and in particular that it acts down to a depth of 3.5 mm in this type of stone and has produced a significant increase in resistance compared to the healthy sample. In the same way the improvement in the resistance in the first millimeter is undoubtedly due to replacement of the gypsum by the CaPs. It is important to point out that of the three application times selected, the best results were achieved by the 60 m sample due to its more homogeneous values, which were also slightly higher than the other two samples studied.

4. Conclusions

In this paper we have studied the applicability of a consolidant treatment based on dibasic ammonium phosphate (DAP), in which the gypsum crust on the altered stones is used as a source of calcium to boost the precipitation of calcium phosphate and in this way consolidate the altered stone and remove the gypsum crust. The results obtained in the different experiments carried out during our research reveal the following interesting aspects:

- The amount of DAP at the 3 M concentration may be excessive as it may produce an increase in the viscosity of the solution and because the saturation and the pH have a direct influence on the precipitation of the calcium phosphate phases. However the slowing-down effect linked to the increase in viscosity also enabled an increase in the penetrability of the consolidant. The

water saturation of the poultice may have had an additional influence on the fissuring process and on the loss of fragments of the film of consolidant, aspects that must be taken into account in future research.

- The application method has only considered a single application of the poultice over different time periods. At short (<40 min) and long (240 min) application times the results we obtained were poor in that some gypsum still remained in the samples or a substantial number of fissures developed, in some cases causing fragments of the film of consolidant to fall off. These problems were less frequent when the 60 min application time was used. For this reason we should analyze the alternative option of carrying out repeated treatments at short application times rather than just a single application. It is also important to point out that as well as varying the number of applications, in future research it would be a good idea to assess their performance at different concentrations of DAP.
- The reaction between DAP and gypsum took place in less than 24 h and appears to have been practically completed in less than a week, regardless of the application time used. This is another positive aspect of this procedure, in that it can be performed in a relatively short space of time.
- We were unable to specifically define the evolution and transition between the different calcium phosphate phases, as they all appeared within the first 24 h. However the most plausible precipitation sequence would be to start from two amorphous phases (ACP1 and ACP2) which would then give rise on the one hand to an octacalcium phase, which later develops into hydroxyapatite, and on the other to the precipitation of the tricalcium phase. At the same time and depending on the conditions of the poultice-stone interface (pH, water saturation of the poultice, concentration of the product and saturation index for each phase), it would precipitate brushite. In fact with the different levels of free calcium recorded in the different solutions we were able to distinguish two states that were linked to the Ca/P ratio that would give rise to some or other calcium phosphate phases. Likewise when we washed the samples, we noted that the excess DAP gave rise to new phases that were poorer in calcium and to new amorphous phases.
- The treatment we applied did not recover the original color of the sample although the color changes were not important in terms of the human eye perception respect to the altered surface by gypsum crust.

- Even though the reaction was completed in a week, the consolidant film appears to continue evolving. In fact after washing the samples and removing the excess DAP and the ammonium sulfate, the film itself became increasingly continuous and homogeneous. A second precipitation of calcium phosphates took place in the fissures, producing new crystals. A second application of the consolidant in the most appropriate conditions could enable these heterogeneities in the consolidant film to repair themselves and the fissures to seal.
- The degree of consolidation obtained remains constant down to a depth of approximately 3.5 mm.
- Under the working conditions studied, the best results were achieved by the 60 min application time.

The initial efficacy of the method for eliminating the gypsum has therefore been demonstrated as has its consolidation capacity by precipitating calcium phosphates, when DAP is combined with the calcium produced by the dissolution of the gypsum and/or carbonated stone substrate.

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