Salt extraction from lime-based mortars: an experimental study using different poultice formulations

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Abstract
The extractive capability of soluble salts in poultices currently used in mortar conservation (Arbocel[TM] plus sepiolite; Arbocel[TM], sepiolite and sand; Westox-Cocoon[®]) were tested to evaluate their efficiency and compatibility with specific mortar substrate. The pore size distribution of the experimental mortar substrate and of the blank dried poultices were preliminarily accomplished by mercury intrusion porosimetry (MIP). Desalination tests were carried out on specifically-formulated mortars after capillary absorption of Na_2SO_4 0.3M solution. The efficiency of salt extraction was measured by means of electrical conductivity meter and ion chromatography. Among the tested products, Westox-Cocoon[®] showed the best performance in terms of the ability to extract soluble salts. It is the only poultice with a porosity distribution characterised by prevalent large macropores (20-30 μm), which guarantees it an extraordinary efficiency in the first phase of the extraction process (wetting/dissolving). This last aspect provides a useful term of comparison for conservators who actually use these products and a base of operational protocol more suitable to the needs of the restoration site.

Keywords: built heritage conservation, mortars, desalination poultice, salt extraction performance

1. Introduction

Salt weathering is a deterioration process that takes place in a variety of environments and affects many classes of natural and artificial porous stone materials [1]. Salts can originate from marine spray, air pollution, moisture/water rising from foundations and treatment with incompatible materials [2]. Durability of historical buildings and artworks depends on their unique mineralogical, chemical and physical qualities (i.e., composition, texture and microstructure) and on the quality of the environment to which they are exposed. Nevertheless, the mechanical action due to polycyclic salt crystallisation is capable of disintegrating even the most resistant stone, leading to different deterioration patterns and causing both physical and aesthetic damage [3, 4].
A common and logical solution to damage by soluble salts is to reduce the salt content in the pore network of natural/artificial stones. Rathgen [5] published the first document about desalination of porous materials in 1915 in which he described the desalination of ancient Egyptian art by the so-called 'bath method' (full immersion of the object in water). Today, the 'bath method' is still widely used to desalinate small portable objects [6]. However, additional difficulties may occur when the substrate from which the salts are extracted are intrinsically soft and/or composed of materials potentially susceptible to water, such as porous stone, lime-based mortar and wall paintings. For this class of materials, alternative methods must be used which are based on specific poultice materials. This latter desalination procedure is based on the application of a wet poultice on the surface of a porous medium, treated in two main phases [7]: 1) the 'wetting phase' in which water is transported by the poultice to the porous substrate where it dissolves the soluble salts that crystallise here as efflorescence and/or subefflorescence and 2) the 'salt extraction phase' in which

the dissolved salt ions migrate in an aqueous solution from the porous substrate into the poultice. Salt migration can occur as the result of two different processes: diffusion and advection [7]. In diffusion-based methods, salts are transported from the substrate to the poultice due to a concentration gradient. For this reason, they are usually extremely slow (weeks or months to achieve an acceptable extraction). Advection is relatively faster and driven by capillary action from the substrate to the poultice during the drying process [8–10]. The advantage of desalination using a poultice is that it introduces less moisture into the stone material compared to other methods.

The poultice method is widely used in the practice of built heritage conservation; however, many parameters influence the efficiency of salt extraction. These parameters are essentially linked to the compositional, textural and ultra-structural nature of the porous substrate and are dependent to some extent on the specific microclimatic conditions and the chemical-physical behaviour of the salts involved [11–13]. This means that the efficiency of any given desalination treatment cannot be predicted or easily controlled. It is thus preferable to carry out preliminary empirical tests. The consequence of these technical difficulties for professional restorers is the lack of a common intervention protocol that can be applied with high reproducibility. Conservators generally apply customised procedures already experienced in well-defined categories of materials and in certain territorial or chronological contexts where they can be applied with the expectation of obtaining satisfactory performance (efficiency and speed of the extractive process) and contraindications (extent of damage to the porous substrate and/or painted surfaces).

This paper aims to evaluate in a comparative way the extraction efficiency of three different commercially-available poultices as applied on a custom-made lime-based mortar. To better address problems frequently encountered at restoration sites, an experimental mortar with a complex stratigraphy (up to three layers of different thickness, texture and composition) was formulated. In particular, the composition of the aggregate, its average grain size and abundance (aggregate/binder ratio) were defined in agreement with the results of previous diagnostic studies concerning historic mortars of Palermo (Sicily) [14-16]. The experimental mortars were subject to impregnation cycles with salt solutions of known concentration, so as to quantitatively control the amount of salt extracted for each of the three different poultices applied. The results derived from this experiment, produced useful indications and offer a reliable intervention protocol for the numerous restoration sites in the historic centre of Palermo, which are renowned for the importance and uniqueness of its architectural heritage.

2. Materials and Methods
2.1 Preparation of mortar specimens

In accordance with what was found through the systematic analysis of the historic mortars of Palermo - where the same recipe was implemented with substantial continuity from the early Middle Ages up through the first decades of the twentieth century [14-16], the stratigraphy of the experimental mortars to be desalted consisted of a succession of three layers: a 'rendering layer ' (8 mm thick) placed directly on the stone substrate (local biocalcarenite) to reduce surface irregularities, a 'floating layer' to bring the plaster into the required true plane (5 mm thick) and a 'finishing layer' (2 mm thick) to provide the desired texture (Fig. 1). The rendering layer, according to historical recipes, has a binder/aggregate ratio of 1:3 (mainly fine to coarse sand sizes between 2 and 0.125 mm), the floating layer has a binder/aggregate ratio of 1:2 (mainly fine to medium sand sizes between 0.5 and 0.125 mm) and the finishing layer has a binder/aggregate ratio of 1:1 (mainly very fine to fine sand sizes between 0.25 and – 0.063 mm). The aggregate was obtained from local littoral sand composed of a carbonate component (bioclasts, biocalcarenite, limestone and dolostone lithic fragments) and a siliciclastic component (quartz, chert, quartzarenite lithic fragments and, minor feldspar), both roughly equally represented. This is the composition found in the historical mortars and plasters of Palermo, which was handed down for over a millennium. For the finishing

layer, fine powdered marble (MK000 variety, i.e., grains with ø = 0.06-0.7 mm by CTS, s.r.l.) was mixed with equal amounts of previously-sieved natural sand in order to obtain a smooth appearance.
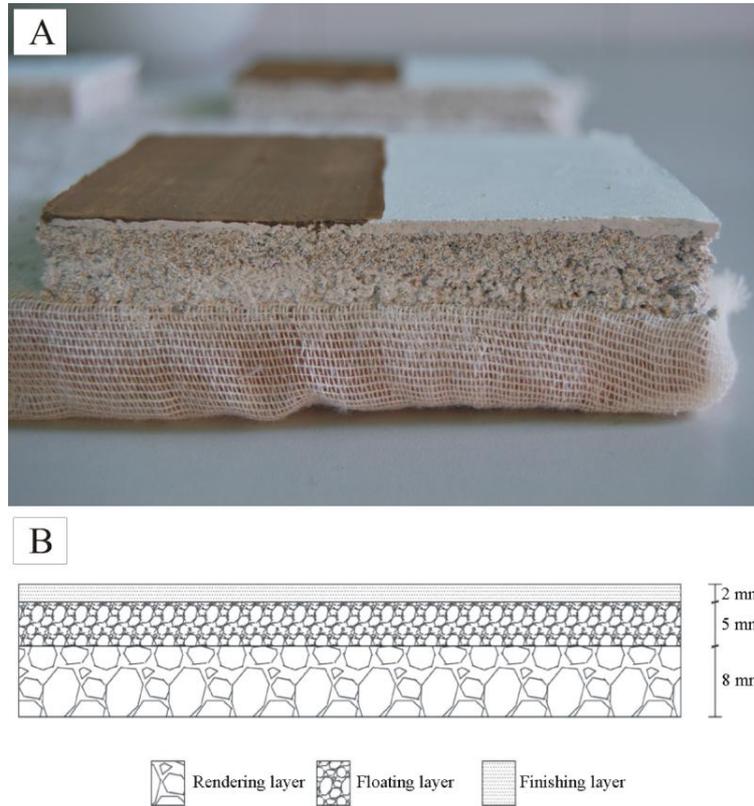
Figure 1. (A-B) Stratigraphy of the experimental plasters.

Table 1 summarises the mineralogical, chemical and granulometric characteristics of the sand used as aggregate in the experimental plasters. A 14-month aged slaked lime putty was used as a binder.

Table 1. Granulometric and chemical characteristics of the sandy aggregate used for the experimental mortar.	
Oxides	weight %
SiO_2	8.06
Al_2O_3	0.5
Fe_2O_3	0.82
MnO	0.01
MgO	2.57
CaO	51.14
Na_2O	0.24
K_2O	0.06
P_2O_5	0.09
LOI	35.4
Total	98.89
Element	ppm
V	7
Ba	1

Sr	973
Y	3
Ni	8
Cu	5
Zn	14
Rb	10
Nb	3
La	9
Ce	26

Sizes [mm]	Freq. [%]
2 - 1 mm	0.06
1 – 0.5 mm	7.26
0.5 – 0.25 mm	65.98
0.25 – 0.125 mm	26.07
0.125 – 0.063 mm	0.63
<0.063 mm	0.01

2.2 Preparation of poultices

The experimental poultices were manufactured using different proportions of clay, powdered cellulose, natural sand and water. The clay component was Pansil 100 by TOLSA, a polyfunctional additive supplied as a fine powder manufactured from sepiolite. The large surface area combined with the high porosity of sepiolite particles ensure significant absorption and desorption properties, which justify its widespread use in the field of conservation. The cellulose-based compound used for the preparation of the experimental poultices was extra-pure finest-grade natural cellulose with average fibres 700 μm in length (Arbocel BC1000 by Rettenmaier & Söhne). The sand fraction consisted of equivalent amounts of very fine sand (0.125–0.063 mm) and fine sand (0.25–0.125 mm) separated after washing and sieving of local littoral sand. Three different formulations were prepared and tested. The first formulation was a mixture of sepiolite/ArbocelBC1000/water (hereafter Treatment A) with a ratio of 1:3:2. A mixture like this is commonly used in restoration practice, specifically on wall painting [17]. The relatively greater amount of cellulose pulp helps to avoid the fast drying of sepiolite powder that could induce the detachment of small fragments from the wall painting. In terms of paste workability, the right amount of deionised water was empirically established.

A certain quantity of sand (the same used for the realisation of the mortar's layers) was added to the second formulation (hereafter Treatment B) in order to improve the efficacy of the extraction treatment (sepiolite/ArbocelBC1000/sand/water, ratio 6:6:6:14). This recipe was employed for a long time by restorers of the *Opificio delle Pietre Dure* (Florence, Italy) for the extraction of salt from wall paintings. It was particularly appreciated for its absorbent qualities, balanced drying times and poor adhesion to the surface.

Both treatments were manually moulded using a steel spatula. First, they were mixed in a dry state to ensure good dispersion of the cellulose fibres, then deionised water was added.

The above described composite poultices were also compared with a premixed product, commercially available (Westox-Cocoon®, Australia). The commercial poultice (hereafter Treatment C) consisted of very fine cellulose fibres, bound to absorbent siliceous earth and, already mixed in distilled water, with the addition of minimum quantities of methylcellulose and 0.1% of preserving additive (product data sheet does not provide further information about the nature and

relative proportions of the main components). The presence of salts in the blank poultices was verified by conductivity measurements and ionic chromatography (Table 2).

Table 2. Conductivity values and ionic species concentration measured in the blank poultices.			
Sample code	Sample weight	Water Volume	Solution conductivity
Poultice A	23.19 g	347.85 ml	163.9 µS/cm
Poultice B	10.54 g	158.1 ml	140.7 µS/cm
Poultice C	4.32 g	64.8 ml	329.8 µS/cm
Japanese Paper	2.52 g	37.9 ml	4.6 µS/cm
Ionic Species	Poultice A	Poultice B	Poultice C
Ca^{2+}	1.944	0.315	0.536
K^+	0.051	0.097	0.06
Mg^+	0.36	0.222	0.304
Na^+	0.794	1.027	0.54
F^-	0.028	0.04	0.028
Cl^-	1.475	0.225	0.131
NO_3^-	0.159	0.054	0.035
SO_4^{2-}	0.256	0.116	0.149
HCO_3^-	1.4	1.3	1.1
Cations	3.15	1.66	1.44
Anions	3.318	1.736	1.443
Water conductivity = 0.4 µS/cm			

2.3 Experimental steps

The experimental mortar briquettes were shaped and sized to 10 x 7 x 1.5 cm. Three specimens were prepared to be treated with each of the three described poultice formulations, for a total of nine individual experimental tests.

The 'rendering layer' (8 mm thick) was spread with a trowel on a slab of local calcarenite previously immersed in water for 24 hours and wrapped in a layer of cotton gauze in order to easily detach the specimens (to be subjected to the analytical routines) from the stone substrate after the experimental run. After 48 hours, the 'floating layer' (5 mm thick) was spread on the previously-scratched rendering surface to allow a better grip. The 'finishing layer' (2 mm thick) was applied on the previous one after 24 hours. The total curing time was 30 days. After complete drying, half of the surface of each plaster specimen was painted to evaluate the efficacy of the desalination treatments and compatibility with the painted surface. A dark colour painting (raw umber) was selected in order to better distinguish soluble salt efflorescences potentially formed after treatment cycles. Moreover, test specimens of each isolated layer (i.e., rendering, floating, finishing) were prepared in order to assess pore size distribution as well as that concerning the whole sample comprising all three layers. After the application of the finishing layer, the specimens were left to age for an additional 10 days, after which, once detached from the stone substrate, they were placed to dry in a ventilated oven at 105 °C, until attaining constant mass.

In order to simulate, in the most realistic way possible, the migration dynamics of the saline solutions in masonry, the experimental test samples were placed in contact with several superimposed layers of absorbent cloths, which in turn are in direct contact with a Na_2SO_4 0.3M aqueous solution (Fig. 2a). In this way, direct contact between the complex stone substrate - mortar and solution was avoided and impregnation by capillary action was strongly enhanced.

The test was interrupted after six days, when the difference between two successive weighs at a 24-hour interval was less than 0.5%. During this time interval, visible salt efflorescence formed on the surface of all the experimental briquettes (Fig. 2b). After this procedure, samples were dried again at 105 °C for 24 hours and weighed (Table 3). The weight acquired by each specimen should therefore correspond to the total amount of salt acquired after the impregnation cycle.

Each poultice formulation was tested on three different specimens (in triplicate) after salt loading. The poultice was applied on the plaster surface (both unpainted and painted parts) with a metal

spatula. A double layer of Japanese paper was previously interposed in order to inhibit detaching and damage of paint film. The Japanese paper was wetted with deionised water before laying the poultice. Treatments A and B were spread with a thickness of 5 mm. Greater thickness caused problems of stability and adhesion on vertical surfaces due to excessive weight. Following the instructions in the technical brochure, Treatment C was applied with a thickness of 10 mm and slightly thicker edges.
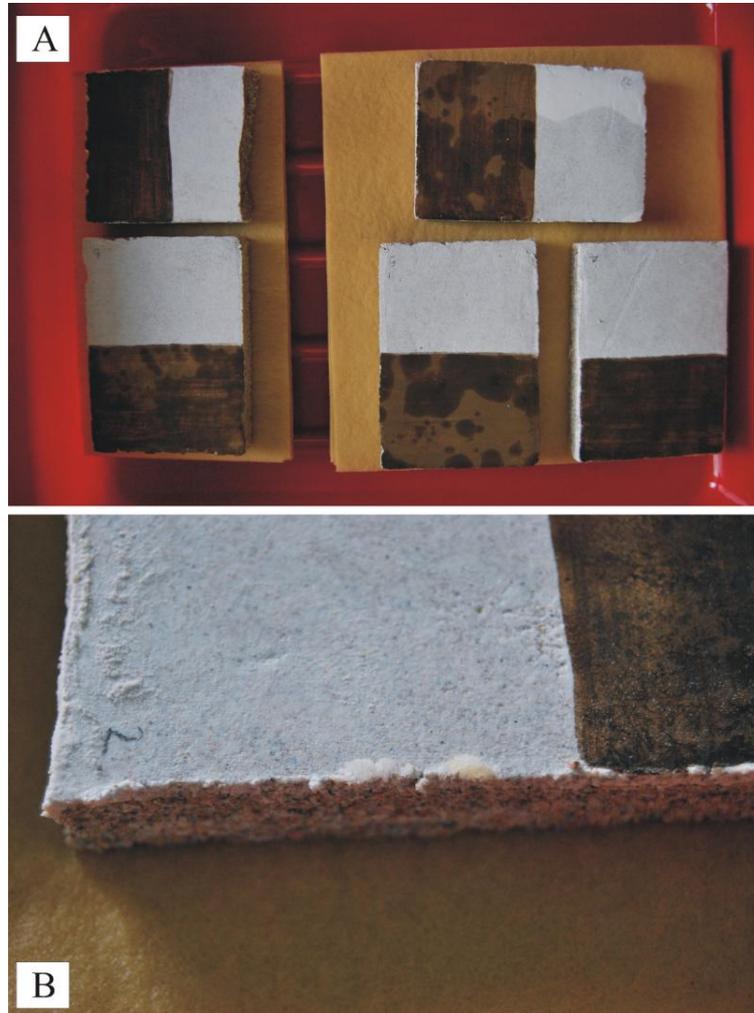
Fig. 2. (A) Impregnation phase by capillarity; (B) salt efflorescences formed on the surface of the experimental mortar briquette.

Table 3. Total salt amount acquired by the experimental poultice treatments after the impregnation cycles.

Sample code	Initial weight [g]	Final weight [g]	Salt content [g]	Salt content [%]
Plaster A.1	194.16	197.88	3.72	1.92
Plaster A.2	187.29	190.79	3.50	1.87
Plaster A.3	172.4	175.92	3.52	2.04
Plaster B.1	193.23	197.49	4.26	2.20
Plaster B.2	187.88	192.06	4.18	2.22
Plaster B.3	135.39	138.18	2.79	2.06
Plaster C.1	193.09	196.69	3.60	1.86
Plaster C.2	188.35	192.7	4.35	2.31
Plaster C.3	196.78	201.42	4.64	2.36

Poultices were left in place until complete dehydration was achieved. After removal, each test poultice was dried in an oven (at 105 °C until constant weight) and re-suspended for 24 hours in a volume of deionised water equal to 15 ml per g of material [18]. Then, conductivity measurements and ionic chromatography were performed following the procedure reported in UNI-EN 11087:2003. The efflorescences were removed with a soft brush, weighted and analysed for the identification of the saline species by scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) and Fourier-transform infrared spectroscopy (FTIR). The process of salt removal was closely monitored and considered ended when the conductivity of each poultice reached values close to those of the respective blank samples. At the end of the procedure, samples of plaster from each set of treatments were taken in order to determine the residual salt content by ionic chromatography.

2.4 Analytical methods

Both plaster specimens and poultices were characterised in terms of pore-size distribution by the technique of mercury intrusion porosimetry (MIP). For this purpose, an Autopore IV porosimeter, by Micromeritics, was used with a pressure range between 25 and 400 MPa and pore size ranging from 0.003 to 40 µm.

The experimental materials were also subjected to SEM-EDS observations performed by an LEO 440 equipped with EDS microanalysis system Link Analytical-Isis. Operating conditions for the micro-morphological observations were 15 kV of accelerating voltage and a 200 pA beam current. Conductivity measurements were performed after each test treatment at 25 ˚C by means of a VWR EC 300 conductimeter. The instrument was calibrated with two standard KCl solutions of certified conductivity (1280 µS/cm and 128 µS/cm).

Ion chromatography was carried out by means of Dionex DX 120 equipment on filtered supernatant (Minisart RC 25 filter, diameter = 0.45 µm). In particular, the following ionic species were analysed: SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, Li^+, Na^+, K^+, Ca^{2+} and Mg^{2+}, with a precision of ±3%. Concentration ranges used for calibration computed with seven calibration points are the following: SO_4^{2-} (0.5-50 mEq/l), NO_3^- (0.2-20 mEq/l), Cl^- (0.5-50 mEq/l), F^- (0.03-3 mEq/l), Br^- (0.05-5 mEq/l), Li^+ (0.02-2 mEq/l), Na^+ (0.5-50 mEq/l), K^+ (0.3-30 mEq/l), Ca^{2+} (0.5-50 mEq/l) and Mg^{2+} (0.3-30 mEq/l). Detection limits for each species investigated in mEq/l were: SO_4^{2-} (0.05), NO_3^- (0.05), Cl^- (0.01), F^- (0.005), Br^- (0.005), Li^+ (0.01), Na^+ (0.05), K^+ (0.05), Ca^{2+} (0.05) and Mg^{2+} (0.05). Additionally, a titration method was used for determining carbonate and bicarbonate concentrations.

Since the analysed specimens were different in shape, size and mass, and were used in different volumes of immersion water, the experimental results were normalised through the multiplying factor V/m, where V is the volume of immersion water (l) and m is the mass (g) of the plaster/poultice. According to Borges and co-author [18], the obtained normalised values give the amount of the ionic species (mg) corresponding to 1 g of plaster/poultice sample. This normalisation procedure permits comparison of the results obtained by means of different experimental runs and procedures.

Fourier-transform infrared spectroscopy (FTIR) measurements were also carried out in order to identify the salt species introduced by the impregnation procedure. Infrared spectroscopy was performed with a TENSOR 27 FTIR spectrometer equipped with a HYPERION 1000 FTIR microscope in the region 4,000–400 cm^{-1} using the ATR method (attenuated total reflectance).

3. Results and discussion
3.1 Microfeatures of mortar substrate and poultices

Blank samples of the experimental mortar and the three poultice formulations were initially characterised by MIP in order to evaluate and compare the corresponding pore-size distributions. In fact, to achieve suitable wetting of material to be desalted, the poultice should have pores larger than the pores in the stone substrate, so that the latter will be able to absorb the amount of water needed to totally dissolve the salts crystallized inside the pore network. For the extraction of the dissolved salts, the poultice should have pores smaller than those of the contaminated stone material so that the advection process can take place. According to these considerations, poultices were designed to be effective in both phases of treatment (initial wetting and desalination), having a satisfactorily-wide pore-size distribution incorporating large pores (acting as water reservoirs for wetting step) and small pores (to ensure advection from the stone substrate to the poultice). Control of the porosimetric distributions of the single layers constituting the mortar as a whole highlighted marked similarities which therefore might guarantee an acceptable connectivity of the pore network, including the painted film (Fig. 3).
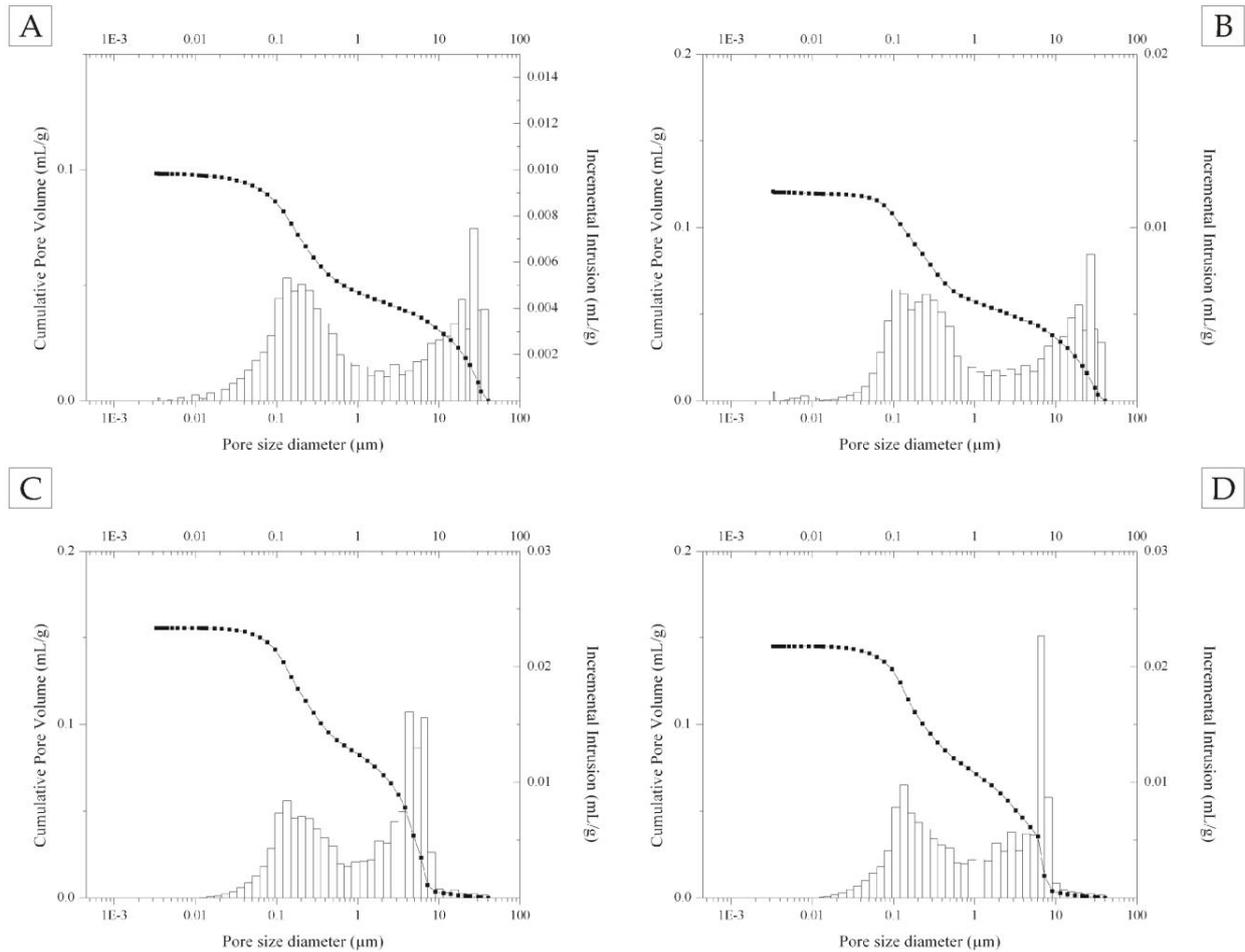
Fig. 3. Pore-size distribution of the blank experimental mortar: (A) rendering layer; (B) floating layer; (C) finishing layer and (D) painted finishing layer.

In particular, both the rendering layer and the floating layer (Fig. 3A-B) show a distinct bimodal distribution, with acceptably coincident modes, respectively equal to 0.1-0.3 μm and 20-30 μm. The finishing layer shows a similar bimodal pore-size distribution, but only as regards the small size macropores (0.1-0.2 μm) while it shows a second mode at 4-6 μm, which is about 5 times less than both rendering and floating layers. There is also no significant difference between the pore-size distributions of unpainted and painted finishing layers.

Figure 4 shows the curves relating to the pore-size distribution (within the range 0.001−100 μm) measured by the MIP technique on the A, B and C poultices before the experimental runs (blank).

Poultice A shows a bimodal pore-size distribution, with a first mode in the large mesopores range (0.02-0.03 □m) and a second significant mode around 10 □m (Fig.4A). Poultice B also shows a bimodal pore-size distribution, similar to the previous one as regards the range of mesopores, although with a certain difference in the second mode in the range of macropores around 4-5 □m, probably as an effect of the addition in the recipe of 20% by volume of fine sand compared to Treatment A (Fig. 4B). Poultice C, although also presenting an evident pore-size distribution of bimodal type, shows marked differences compared to the previous ones. In fact, contrary to what was found for poultices A and B, the modal class in the mesopores range at 0.02-0.03 □m is absent (Fig. 4C).
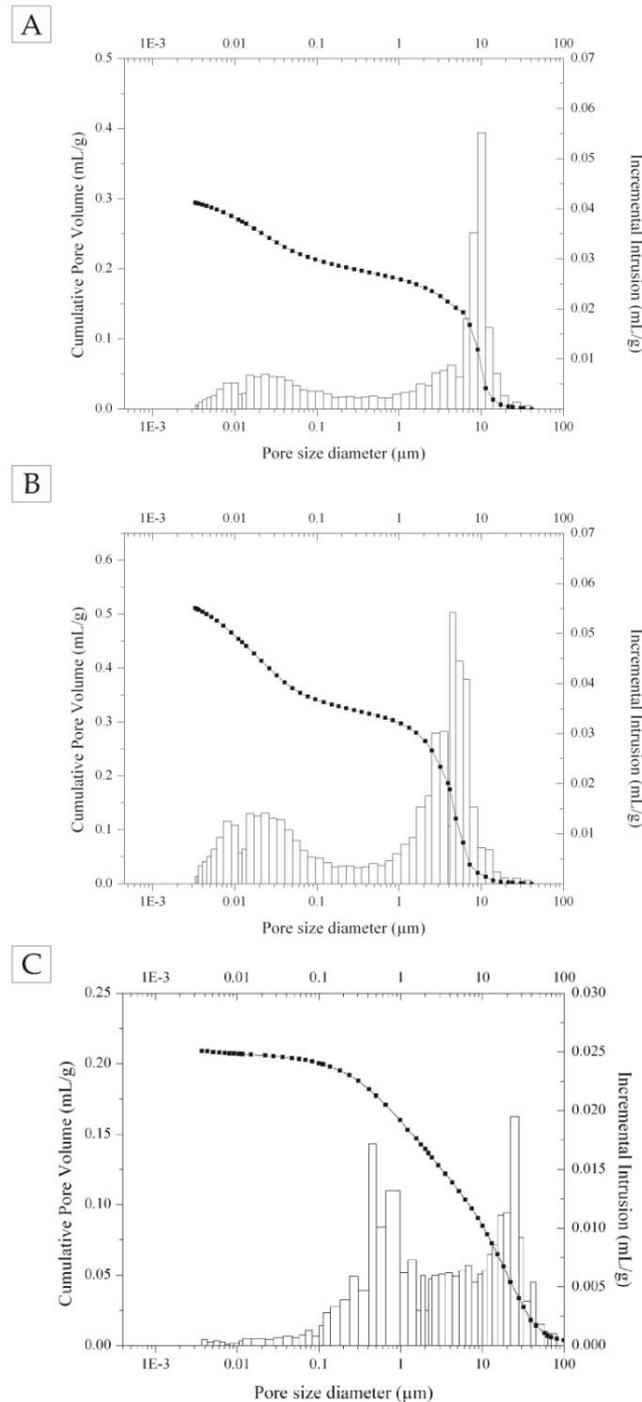
Fig. 4. Pore-size distribution of the blank experimental poultices: (A) poultice A; (B) poultice B; (C) poultice C.

The first mode of poultice C falls instead in the range of small macropores (0.5-0.8 □m). The pore range between 1 and 10 mm is also well represented, while the second mode falls between 20-30 □m, as in the porosimetric distributions of both rendering and floating layers of the experimental mortar. The relatively greater frequency of pores with diameters between 5 and 30 μm could be relevant for the wetting phase. As already specified above, poultice C was not prepared experimentally since it is a ready-for-use desalination poultice. As reported in the technical sheet and confirmed by SEM-EDS observations, this product is composed of diatomaceous earth and small cellulose fibres (average 0.5 □m) mixed with pure water (Fig. 5). It is well known that diatoms are unicellular silica-like algae that live both in the seas and in freshwater. They vary in diameter by three orders of magnitude, from cells that over 2 mm in diameter down to species with cells with diameters of 2 μm. Furthermore, their shells are characterised by the presence of very small pores, from 0.1 to 0.01 □m.
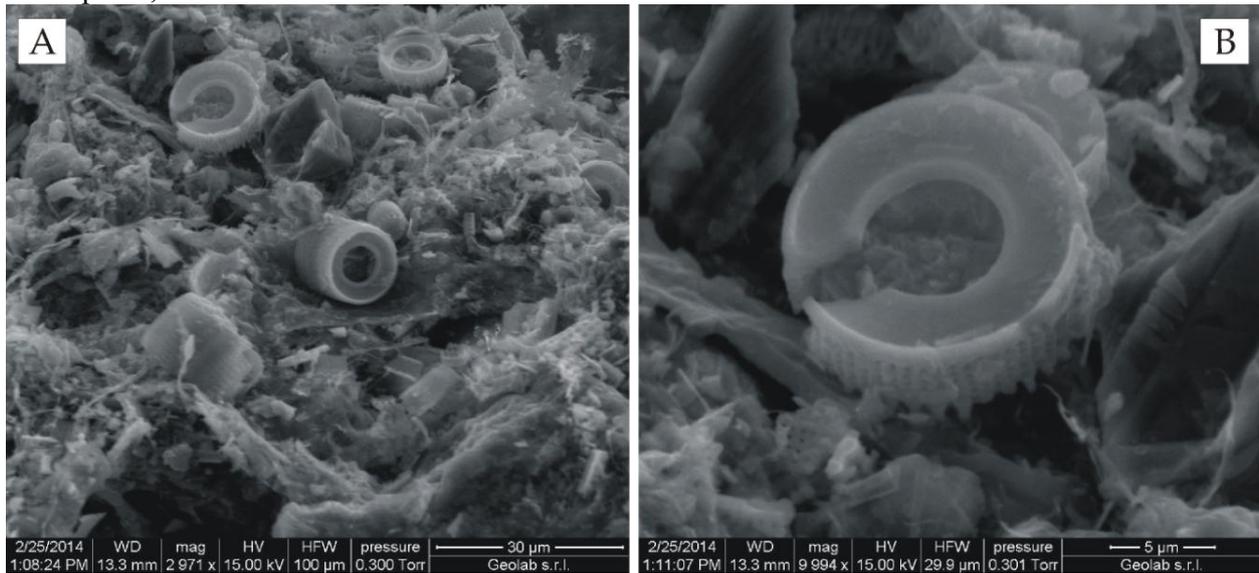
Figure 2. (A-B) SEM-SE microphotographs of poultice C showing diatomaceous earth and small cellulose fibres.

3.2 Description of macroscopic effects of salt removal treatments

A first important evaluation of the desalination treatment consists in the macroscopic examination of the effects produced on the surfaces. This step is used by conservators as an empirical verification of the progress of the extraction process and detection of unwanted side effects. In case of treatment B, 16 hours after the first application, the poultices (and the three replicates) partially lifted while still wet (Fig. 6a). This specific behaviour could negatively affect the extraction processs, which usually requires a longer curing time. After 48 hours, the samples were totally dry (Fig. 6b), and therefore, they were removed from the stone substrate. During removal, along the edges of specimens, where poultice no longer adhered, salt efflorescences were detected (Fig. 6c). Treatment A (all three replicates), on the other hand, showed no signs of detachment, even when completely dried, three days after its application to the mortar substrate. These tests, on the contrary, suffered evident shrinkage leaving the margins of the specimens uncovered (Fig. 6d). Treatment C had the highest water content, so it immediately and visibly impregnated the whole mortar substrate. The replicas took a longer time to dry (8 days); after that, they detached completely (Fig. 6e). Evidence of salt efflorescence was observed, especially along the external border of the specimens (Fig. 6f).

From the second application onwards, treatments A and B produced similar results in terms of drying behaviour in that drying times became longer, 6 and 7 days, respectively, and regularised. Treatment C, on the other hand, took an average of 11 days to dry completely, in good agreement with what is specified in the technical data sheet provided by the manufacturer.
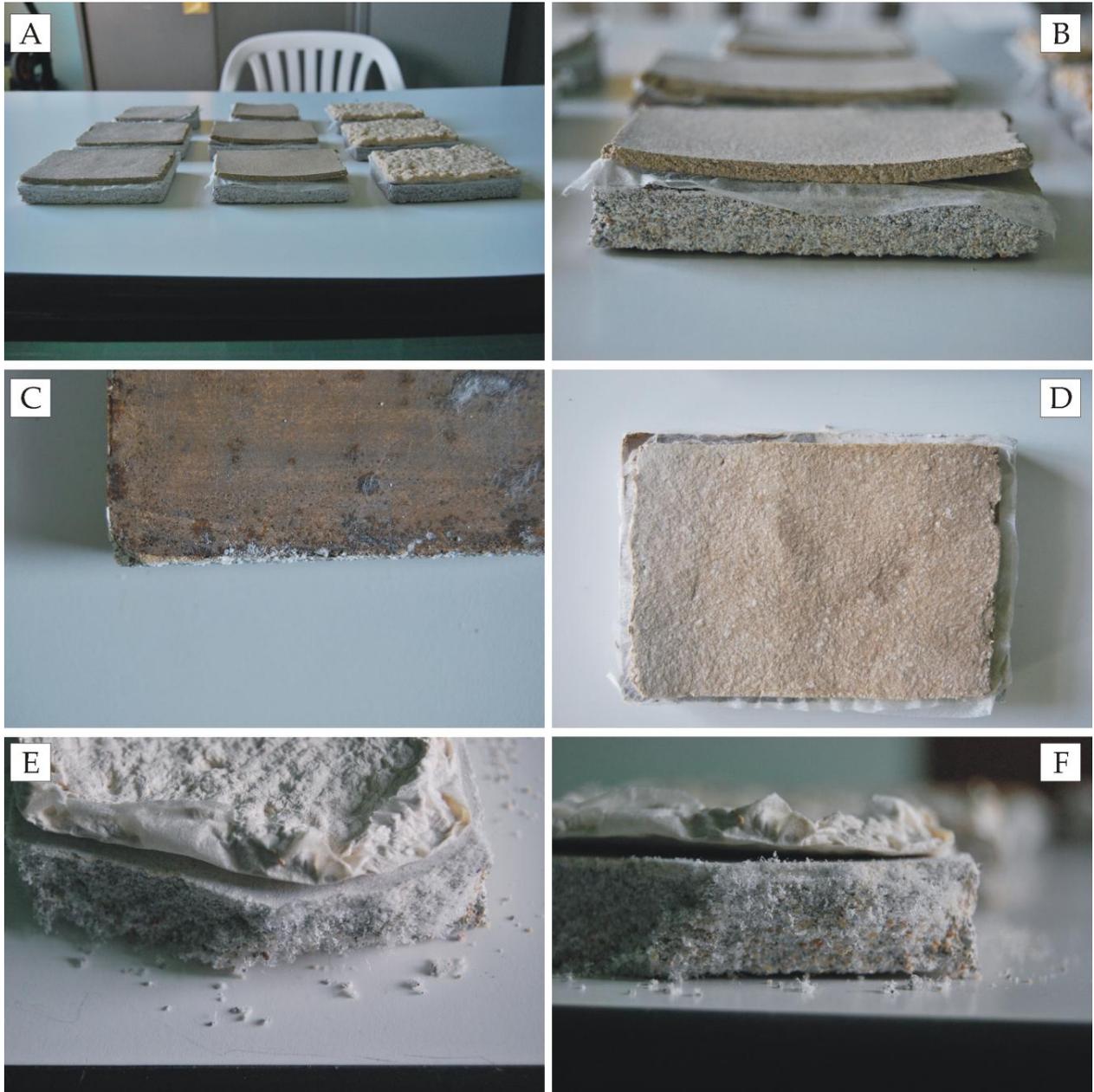
Fig. 6. (A) Macroscopic appearance of the experimental mortar after 16 hours from the first application and after 48 hours (B); (C) salt efflorescences detected at the edge of the specimen; (D) shrinkage experienced by the Treatment A; (E) detachment of the Treatment C after drying and (F) evidences of salt efflorescences along the external border of the mortar test specimen.

At the end of the treatments, mortar specimens subjected to the soluble salt extraction procedure (treatment C) were those that, contrary to the beginning, had a lower quantity of efflorescences, which were sporadically found only at the edges of the outer surface. On the other hand, salt efflorescences were clearly more frequent on specimens treated with poultice A and, to a slightly lesser extent, in poultice B (Fig 7a). They affected the surface and were diffused evenly throughout the external border. This effect might indicate that the extraction of soluble salts has not been entirely successful. In fact, the saline solution has migrated from the core of the mortar substrate (inner layers) towards its surface although the transport of the salts toward the poultice was not completed due to rapid drying. In some replicas, clear separations between the compositional layers of the test mortar were found (Fig. 7b). The precipitation of salts is likely related to changes in porosity at the interface between the rendering layer and the floating layer, with greater frequency

of small-diameter capillary pores in the floating layer. This may cause an increase of crystallisation pressures and consequently, intergranular decohesion of the binder (Fig. 7c).

With regard to the effects to the surface, formulation A was the most aggressive, showing detachment of flakes from the painted finishing layer (Fig. 7d). In treatment C, the above-described side effects (efflorescence and subefflorescence) were not observed at all, only small superficial cracks (Fig. 7e). However, mildew growth was detected likely due to the presence of methylcellulose and relatively higher water content in this poultice (Fig. 7f).
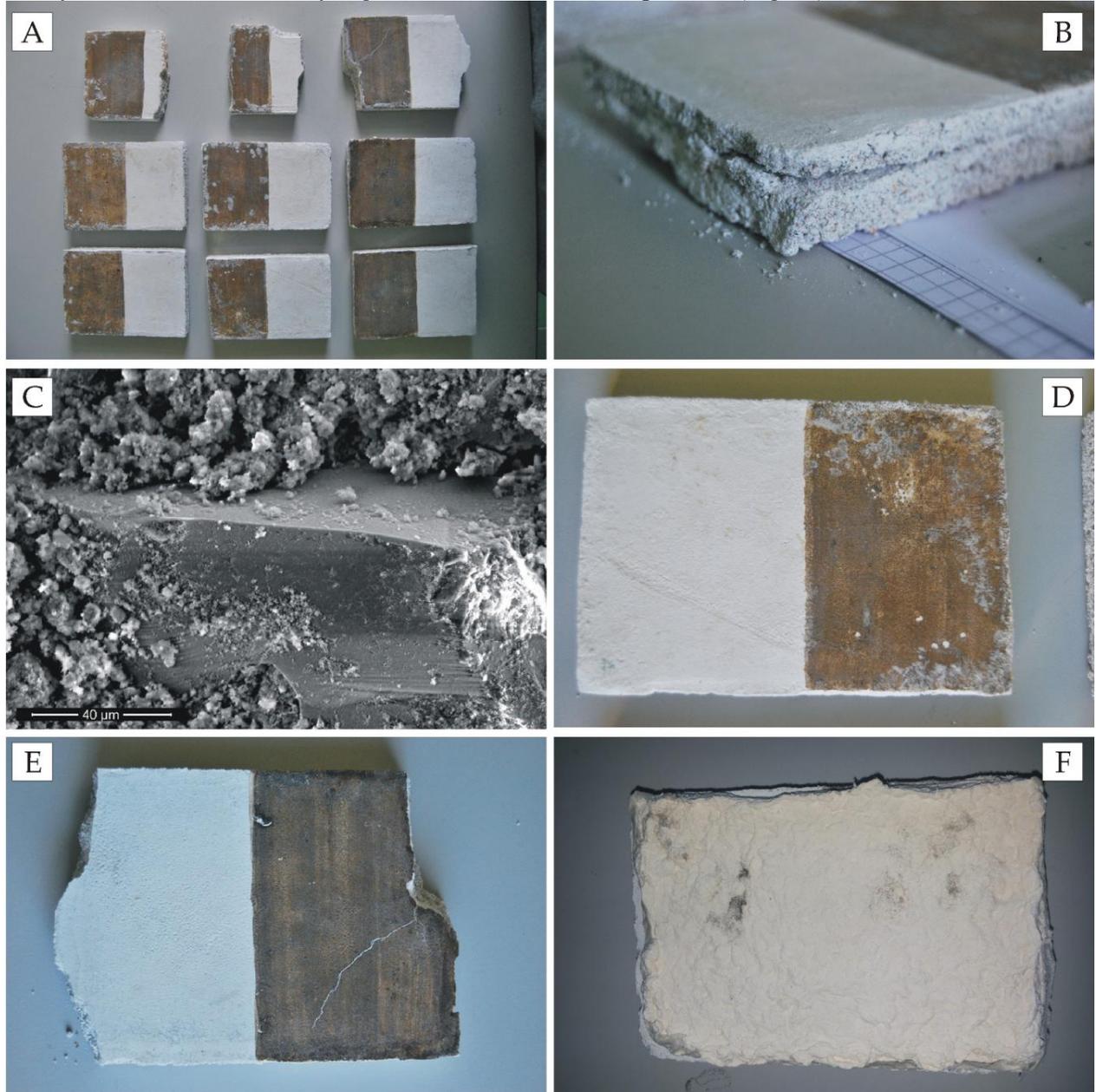
Fig. 7. (A) Salt efflorescences evidences on treated mortar test specimen; (B) clear separation between the composing layers of the mortars; (C) Intergranular decohesion of the binder by SEM-SE imaging; (D) flakes detachment from the painted finishing layer; (E) small superficial cracks on specimen treated with C poultice; (F) mildew growth detected on specimen treated with C poultice.

3.3 Conductivity patterns of extractive tests

An initial evaluation of the effectiveness of extraction treatments was made using conductivity measurements. Each of the three treatments, performed for a total of six successive applications,

showed quite different trends in terms of extraction efficiency indirectly estimated by conductivity values measured in the supernatant (Table 4). As can be seen in Figure 8, starting with the first application of poultice Treatment C, the conductivity values were about 40 times higher than Treatment B and about 30 times than Treatment A. In subsequent applications (experimental runs 2-6), no significant changes, compared to the first extraction, were detected for treatments A and B, except for a slight decrease in the last extraction (relatively more significant for poultice B).
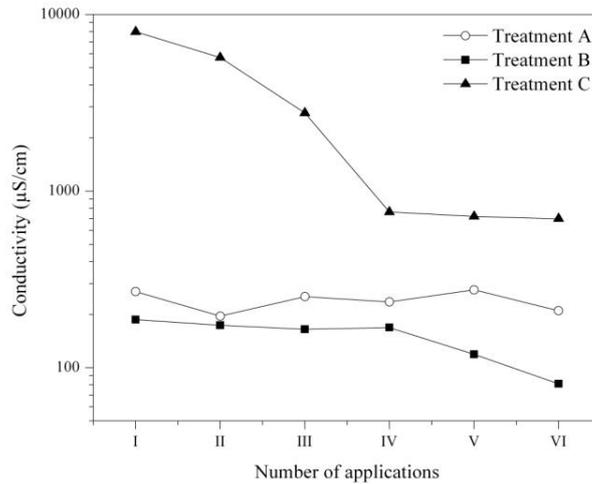
Figure 3. Pattern of the extractive tests.

Table 4. Conductivity values measured in the extractive tests.

Number of applications	Treatment A				Treatment B				Treatment C			
	Conductivity (µS/cm)											
	1	2	3	Mean	1	2	3	Mean	1	2	3	Mean
I	248	256	270	258	187	163	166	172	5473	7960	7986	7140
II	176	192	196	188	189	174	190	184	3441	5527	5709	4892
III	253	258	305	272	179	133	165	159	2776	4528	2769	3358
IV	327	340	365	344	169	235	237	214	1001	1444	762	1069
V	276	341	424	347	107	112	119	113	940	1524	720	1061
VI	236	285	210	244	101	81	111	98	883	1567	698	1049

 In all of the applications steps, treatment with poultice C proved to be more efficient than either treatment A or B. In particular, there was a constant decrease in conductivity values from the first to the fourth extraction (notably different from the other treatments), although the latter was still remarkable in absolute value. From the IV application to the VI, the conductivity values were substantially constant and up to eight times higher than those obtained with the A and B poultices. It is important to note that a regular decrease in conductivity values in subsequent applications is considered one of the requisites necessary to define an effective desalination treatment [19]. However, based on previous reports, irregular decreasing trends in conductivity values are not sporadic events [19]. Therefore, given that all the extraction tests in this study were conducted under identical operating conditions, on the basis of the conductivity values, it can be stated that treatment C extracts much higher amounts of salt than the other two treatments, and that treatment B was the least effective.

3.4 Identification and quantification of extracted salts

Although the solution used for impregnation consisted only of Na$_2$SO$_4$, the presence of other crystalline species was investigated as well. In fact, it is well known that starting from anhydrous sodium sulphate (thenardite), through dissolution and reprecipitation cycles, decahydrate sodium sulphate (mirabilite) can form in the efflorescence and sub-efflorescence. This last crystalline phase, due to an increase of more than four times the molar volume as a result of hydration, is able to exert very high pressures inside the capillary pores and leading to decohesion of the mortar body [20]. Therefore, FTIR analyses were carried out on salt deposits collected after the removal of the various poultices (EF-1) and directly from the mortar specimens (EF-2). The spectra obtained almost overlap with both showing the presence of thenardite (Fig. 9a–b). In fact, it is possible to observe the band, typical of sulphates, which corresponds to strong S–O stretching in the 1200–1050 cm^{-1} range. Another small band present near 1000 cm^{-1}, is given by the bending vibrations, together with slightly stronger and narrower bands at 700–600 cm^{-1}. The O–H stretched hydrogen bond at 3500–3200 cm^{-1} is absent, which excludes the presence of mirabilite. Calcite was also detected in both samples, as shown by the absorption bands, which are symmetrical and wide, given by the stretching of the C-O bond in the region of 1550–1350 cm^{-1}, the narrow bands in the region 900–650 cm^{-1} are produced by the bending vibrations of the carbonate, in particular, the bending vibration at 872 cm^{-1}. This latter mineralogical phase certainly derives from small binder particles accidentally collected after manual scraping of salt efflorescence.
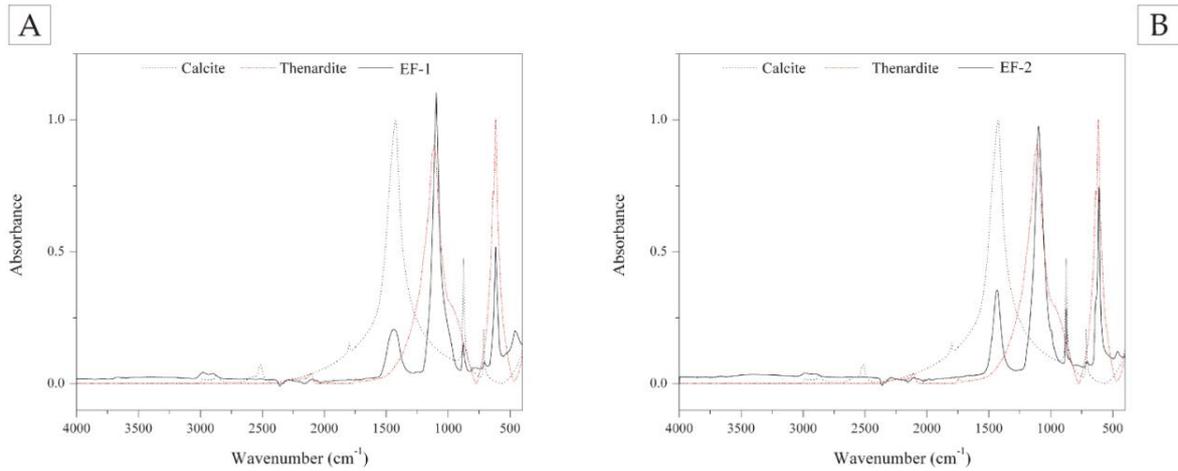
Fig. 9. FTIR spectra of neoformed salt efflorescences: (A) EF-1 collected after the removal of the various poultices and (B) EF-2 collected directly from the mortar specimens.

The quantification of ionic species contained in mortar specimens before, during and after each treatment was achieved by ion chromatography. The ionic species and the relative concentrations found in each of these materials, expressed as mEq/l, are reported in Table 5.

Table 5. Concentrations (in mEq/l) of the ionic species removed from mortar test specimens before, during and after each desalinization treatment.

Sample code	Ca^{2+}	K$^+$	Mg$^+$	Na$^+$	F$^-$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	HCO$_3^-$	Cations	Anions
Raw Plaster	0.313	0.002	0.008	0.009	0.001	0.024	0.004	0.010	0.300	0.333	0.339
Saturated Plaster	1.749	0.000	0.003	0.297	0.002	0.022	0.004	0.406	1.800	2.050	2.233
Deionized Water	0.001	0	0	0	0	0.020	0	0.007	0	0.001	0.027
Treatment A (raw)	0.315	0.097	0.222	1.027	0.040	0.225	0.054	0.116	1.300	1.660	1.736
A-I.1	0.370	0.060	0.161	1.928	0.021	0.285	0.039	1.160	0.900	2.519	2.405

A-I.2	0.369	0.066	0.135	2.060	0.030	0.248	0.036	1.181	1.100	2.631	2.595
A-I.3	0.387	0.069	0.132	2.159	0.041	0.213	0.006	1.355	1.000	2.747	2.615
A-II.1	0.395	0.077	0.205	0.988	0.043	0.132	0.041	0.346	1.150	1.665	1.713
A-II.2	0.404	0.077	0.225	1.138	0.044	0.140	0.040	0.449	0.650	1.843	1.323
A-II.3	0.523	0.078	0.188	1.126	0.050	0.151	0.035	0.483	1.350	1.914	2.069
A-III.1	0.430	0.083	0.175	1.768	0.043	0.175	0.037	0.990	1.350	2.457	2.594
A-III.2	0.449	0.078	0.186	1.877	0.043	0.174	0.035	1.149	0.700	2.590	2.102
A-III.3	0.519	0.086	0.233	2.277	0.049	0.165	0.035	1.528	1.500	3.114	3.277
A-IV.1	0.465	0.076	0.212	2.606	0.043	0.159	0.027	1.637	1.400	3.359	3.266
A-IV.2	0.462	0.074	0.189	2.707	0.044	0.158	0.030	1.765	1.550	3.431	3.547
A-IV.3	0.555	0.135	0.273	2.683	0.058	0.210	0.029	1.977	1.500	3.646	3.774
A-V.1	0.501	0.115	0.232	2.155	0.045	0.184	0.030	1.514	1.300	3.003	3.073
A-V.2	0.408	0.065	0.148	3.202	0.050	0.163	0.030	2.031	1.700	3.823	3.975
A-V.3	0.679	0.095	0.358	3.565	0.053	0.193	0.036	3.010	1.550	4.696	4.843
A-VI.1	0.409	0.070	0.279	1.853	0.041	0.132	0.025	1.169	1.300	2.610	2.667
A-VI.2	0.416	0.075	0.294	2.310	0.043	0.173	0.030	1.670	1.400	3.095	3.316
A-VI.3	0.447	0.079	0.355	1.478	0.052	0.150	0.028	0.792	1.450	2.359	2.473
Treatment B (raw)	0.536	0.060	0.304	0.540	0.028	0.131	0.035	0.149	1.100	1.440	1.443
B-I.1	0.428	0.060	0.202	1.307	0.036	0.095	0.017	0.800	1.100	1.997	2.049
B-I.2	0.351	0.053	0.166	1.158	0.032	0.089	0.018	0.593	0.900	1.728	1.631
B-I.3	0.410	0.061	0.213	1.067	0.037	0.098	0.018	0.533	1.100	1.751	1.785
B-II.1	0.539	0.070	0.277	1.151	0.028	0.101	0.010	0.720	1.300	2.037	2.158
B-II.2	0.397	0.059	0.201	1.127	0.027	0.095	0.013	0.653	1.100	1.783	1.889
B-II.3	0.530	0.063	0.308	1.052	0.031	0.084	0.007	0.586	1.200	1.953	1.907
B-III.1	0.485	0.059	0.190	1.089	0.025	0.113	0.015	0.720	1.000	1.824	1.871
B-III.2	0.440	0.052	0.153	0.743	0.022	0.100	0.015	0.420	0.900	1.388	1.457
B-III.3	0.507	0.058	0.229	0.853	0.029	0.089	0.015	0.473	1.100	1.646	1.706
B-IV.1	0.368	0.046	0.160	1.118	0.020	0.082	0.015	1.347	0.900	1.692	2.364
B-IV.2	0.337	0.045	0.139	1.719	0.028	0.072	0.013	1.077	0.900	2.239	2.090
B-IV.3	0.474	0.048	0.172	1.534	0.020	0.082	0.015	1.347	1.200	2.227	2.664
B-V.1	0.330	0.040	0.172	0.614	0.023	0.053	0.014	0.341	0.900	1.157	1.332
B-V.2	0.324	0.041	0.165	0.645	0.024	0.052	0.015	0.372	0.900	1.174	1.363
B-V.3	0.471	0.048	0.181	0.655	0.030	0.075	0.016	0.270	1.000	1.355	1.392
B-VI.1	0.309	0.040	0.166	0.550	0.021	0.046	0.012	0.310	0.800	1.065	1.192
B-VI.2	0.303	0.028	0.114	0.412	0.017	0.044	0.016	0.253	0.600	0.857	0.929
B-VI.3	0.400	0.050	0.236	0.590	0.031	0.052	0.013	0.261	1.000	1.276	1.357
Treatment C (raw)	1.944	0.051	0.360	0.794	0.028	1.475	0.159	0.256	1.400	3.150	3.318
C-I.1	0.102	0.197	0.020	64.642	0.040	1.965	0.173	33.778	23.000	64.962	58.957
C-I.2	0.087	0.242	0.022	96.181	0.029	2.197	0.234	62.427	24.000	96.531	88.887
C-I.3	0.069	0.243	0.019	100.881	0.029	1.773	0.055	61.176	27.200	101.212	90.233
C-II.1	0.064	0.144	0.018	36.199	0.060	1.967	0.181	18.522	17.200	36.425	37.938
C-II.2	0.123	0.184	0.024	61.820	0.066	2.046	0.164	44.200	17.500	62.150	64.001
C-II.3	0.058	0.194	0.022	63.736	0.030	1.730	0.162	37.045	24.500	64.009	63.467
C-III.1	0.061	0.125	0.021	28.620	0.057	1.947	0.000	13.832	15.300	28.827	31.142
C-III.2	0.094	0.164	0.032	48.827	0.047	1.930	0.254	33.286	14.800	49.117	50.327
C-III.3	0.072	0.121	0.023	29.341	0.058	1.783	0.044	12.605	16.700	29.556	31.194
C-IV.1	0.095	0.073	0.036	10.925	0.055	1.692	0.039	4.128	4.500	11.130	10.422
C-IV.2	0.158	0.092	0.071	17.480	0.050	1.778	0.008	11.667	4.300	17.800	17.811
C-IV.3	0.095	0.058	0.027	7.853	0.032	1.262	0.049	2.900	4.100	8.033	8.359
C-V.1	0.315	0.205	0.025	13.336	0.036	1.623	0.137	3.441	7.000	13.881	12.242
C-V.2	0.240	0.082	0.019	18.606	0.043	1.591	0.027	8.774	8.000	18.947	18.442
C-V.3	0.253	0.062	0.019	8.488	0.018	1.325	0.127	1.766	6.000	8.823	9.243
C-VI.1	0.285	0.185	0.018	12.266	0.031	1.433	0,134	3,344	6.657	12.754	11.599
C-VI.2	0.232	0.076	0.021	16.546	0.032	1.443	0,023	7,544	7.654	16.875	16.696
C-VI.3	0.243	0.043	0.017	8.445	0.034	1.423	0,137	1,667	5.543	8.748	8.804

Based on these data and a comparative evaluation, the remarkable extraction power of poultice C was confirmed once again. The data are shown in the binary diagram of Figure 10, which confirms that poultice C extracted a quantity of salt up to two orders of magnitude higher than that extracted with the sepiolite-based treatments. At the same time, the relatively lower extraction capacity of treatment B was established, likely related to the premature detachment of the poultice (Fig. 5a).
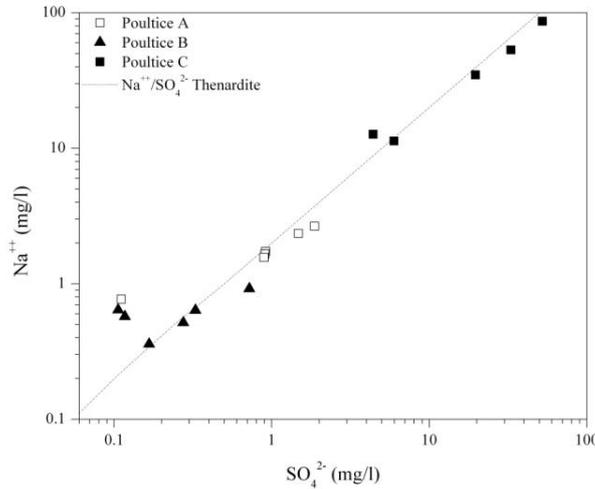
Fig. 10. Binary diagram Na^+ *vs* SO_4^{2-} concerning the performed treatments.

In order to try to quantify the efficiency (ε) of the tested removal treatments, the amount of salt present on the substrate before and after the extractive treatments were compared applying the following equation:

$$\varepsilon = \frac{|\Delta m|}{m_0} * 100 \, ,$$

where Δm (kg) is the mass difference in the amount of salt in the substrate before and after extraction, and m_0 (kg) is the initial mass of the salt content. Efficiency values calculated for the three treatments A, B and C were 32.98, 25.34 and 61.23%, respectively, thus confirming superior extractive capability with Treatment C.

4. Conclusions

Removal of soluble salts from porous substrates has been repeatedly addressed in the field of conservation of built heritage, considering that salts are recognised as one of the main deterioration agents of natural and artificial stone materials. While the scientific research community seeks to better understand the complex mechanisms by which the pressure generated by the crystallisation of salts is triggered, conservators face the practical aspects involved in the daily choice of treatments and procedures.

The present study analysed the performance of three different extractive poultices in relation to a given stone substrate. Three formulations commonly adopted in the conservation of built heritage sites include: Arbocell®/sepiolite in a 3:1 ratio (Treatment A), Arbocell®/sepiolite/sand in a 6:6:6 ratio (Treatment B) and a pre-formulated ready-to-use product by Westox-Cocoon® (Treatment C). To this end, a custom-formula mortar substrate was prepared simulating the recipes used in the historic mortar of Palermo. It was then impregnated with a 0.3M saline solution of sodium sulphate. In this way, it was possible to quantify the initial salt content, which is essential for assessing the efficiency of the three different poultices.

All of the extractive treatments were effective overall, but there were marked differences in terms of specific performance. Treatment C was comparatively more effective in terms of the quantity of

16

salts extracted after the impregnation cycles, as evidenced by conductivity and ionic chromatography.

The behaviours of the tested poultices are attributed to their respective porosimetric characteristics in comparison with those of the mortar substrate. In fact, treatment C was the only one to have a porosity distribution characterised by a modal class of large macropores (20–30 µm), which guarantees it an extraordinary efficiency in phase 1 of the extraction process (wetting/dissolving). This last aspect provides a useful term of comparison for conservators who use these products and a base of operational protocol more suitable to the needs of the restoration site. In specialised literature, greater emphasis is often given to phase 2 of the process (extraction), guided by macropores with good capillary activity (1–0.05 µm) and by mesopores. However, even on the basis of what has been achieved in this experimentation, before the soluble salts inside the stone material are extracted, they must be completely dissolved and treatment C proved to be more than an order of magnitude higher than the other experimental poultices.

We are aware that a real system, which is more extensive and complex, is not isolated and circumscribed as in the 10 x 7 x 1.5 cm experimental mortar substrate used herein, therefore quantifiable results will change. In this case, the external environmental parameters should be carefully considered, with apparent repercussions on the moisture content of the system, up to and possibly reversing the gradient between the mortar and the extractive poultice, with the potential to generate a soluble salt backflush. Furthermore, the choice of a poultice is based on the practical needs of the specific conservation site, that is to say, the best compromise between extraction capacity, ease of application, tightness, compatibility with substrate and cost/benefit ratio. In conclusion, these experimental data could allow the development of procedures for precise geographical and/or chronological contexts, where the 'recipes' of historic mortars have already been attested.

Acknowledgments

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Highlights

- Soluble salts extractive capability of commercial poulticing materials currently used for historic mortar conservation.
- The pore-size distributions of the mortar substrate and the poulticing material influence the efficiency of the reduction of the soluble salts content.
- The obtained data provide an operating protocol for the restoration sector.

*Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CRediT author statement:

L. Randazzo: Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing; **G. Montana:** Writing - Review & Editing, Conceptualization, Validation, Supervision; **A. Castiglia:** Formal analysis, Investigation, Writing - Original Draft; **M.F. La Russa**: Conceptualization, Supervision