

Materials and Structures

Addition of ferrocyanide-based compounds to repairing joint lime mortars as a protective method for porous building materials against sodium chloride damage --Manuscript Draft--

Manuscript Number:	MAAS-D-20-00826R1	
Full Title:	Addition of ferrocyanide-based compounds to repairing joint lime mortars as a protective method for porous building materials against sodium chloride damage	
Article Type:	Original Research	
Keywords:	preventive treatment; salt damage; crystallization modifiers; lime mortar; ferrocyanide.	
Corresponding Author:	Jorge Feijoo, PhD Instituto de Geociencias Vigo, Pontevedra SPAIN	
Corresponding Author Secondary Information:		
Corresponding Author's Institution:	Instituto de Geociencias	
Corresponding Author's Secondary Institution:		
First Author:	Jorge Feijoo, PhD	
First Author Secondary Information:		
Order of Authors:	Jorge Feijoo, PhD	
	Duygu Ergenç, PhD	
	Rafael Fort, PhD	
	Mónica Álvarez de Buergo, PhD	
Order of Authors Secondary Information:		
Funding Information:	Ministerio de Economía y Competitividad (BIA2014-53911-R)	Not applicable
	Comunidad de Madrid (P2018/NMT-4372)	Not applicable
	Ministerio de Ciencia, Innovación y Universidades (Juan de la Cierva grant)	Mr. Jorge Feijoo
Abstract:	Soluble salts are considered one of the main agents in weathering of porous materials used in building constructions. In this work, a comparison in terms of protection against the damage caused by salts, durability and harmful effects of the application of a joint lime repair mortar, with and without $K_4Fe(CN)_6$ in its composition, for bonding sandstone blocks contaminated with NaCl was evaluated. Results show that the introduction of ferrocyanide allowed: 1) to protect the mortar during the curing process, hindering the entry of salts into its pores during drying; 2) to improve the carbonation of the mortar and its adhesion to the porous materials' surface and 3) to remove chlorides from the surrounding materials, reaching percentages of reduction close to 100%. All of these without causing aesthetic damage to the materials and maintaining a protective capacity against NaCl over time that allows considering this treatment not only as a shock treatment but also as a preventive measure.	
Response to Reviewers:	Editor Comments The paper is very good, and original, but the authors really need to consider all comments to have the paper accepted. In particular, they need to modify their approach to desalination process. There is no validation of desalination by using surface methods. AUTHORS: Firstly, we would like to indicate that the validation of the method as a desalination	

[Click here to view linked References](#)

**Addition of ferrocyanide-based compounds to repairing joint lime mortars as a
protective method for porous building materials against sodium chloride damage**

Jorge Feijoo*

*Ph.D. Defense University Centre, Spanish Naval Academy, Plaza de España, s/n,
Marín, 36920, Spain. jfeijoo@tud.uvigo.es ORCID 0000-0003-3820-5127*

Duygu Ergenç*

*Ph.D. Department of Civil Engineering, Middle East Technical University, 06800
Ankara, Turkey. duyguerg@ucm.es ORCID 0000-0001-9034-1818*

Rafael Fort

*Ph.D. Institute of Geosciences IGEO (CSIC/UCM), c/Doctor Severo Ochoa, 7, 28040,
Madrid, Spain. rafael.fort@csic.es ORCID 0000-0001-9967-2824*

Mónica Álvarez de Buergo

*Ph.D. Institute of Geosciences IGEO (CSIC/UCM), c/Doctor Severo Ochoa, 7, 28040,
Madrid, Spain. alvarezm@geo.ucm.es ORCID 0000-0002-7520-2390*

* Corresponding author

ABSTRACT

Soluble salts are considered one of the main agents in weathering of porous materials used in building constructions. In this work, a comparison in terms of protection against the damage caused by salts, durability and harmful effects of the application of a joint lime repair mortar, with and without $K_4Fe(CN)_6$ in its composition, for bonding sandstone blocks contaminated with NaCl was evaluated. Results show that the introduction of ferrocyanide allowed: 1) to protect the mortar during the curing process, hindering the entry of salts into its pores during drying; 2) to improve the carbonation of the mortar and its adhesion to the porous materials' surface and 3) to remove chlorides from the surrounding materials, reaching percentages of reduction close to 100%. All of these without causing aesthetic damage to the materials and maintaining a protective capacity against NaCl over time that allows considering this treatment not only as a shock treatment but also as a preventive measure.

KEYWORDS: preventive treatment, salt damage, crystallization modifiers, lime mortar, ferrocyanide.

1. Introduction

Built cultural heritage, and also modern structures, is continuously exposed to several alteration factors, both natural and anthropogenic, that makes in some cases its preservation at serious risk. Among these alteration factors, soluble salts induced decay is a major issue of interest within the field of heritage conservation since is one of the most widespread cause of damage [1–5].

Damage caused by this agent depends on the zone of the material where they crystallize:

1) On its surface, as efflorescence, the damage is merely aesthetic, since they do not

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46 exert any pressure against the pore's wall. 2) Beneath the material surface, as sub- and
47 crypto-efflorescence, severe damage may occur since salts can cause internal pressures,
48 due to crystallization, hydration and thermal expansion processes against the pore's
49 walls that can exceed the tensile strength of the material. In consequence, the loss of
50 part of the material in the form of blistering, scaling (flaking and spalling),
51 alveolization, crumbling and granular disintegration (powdering and sanding)
52 (terminology according to [6]) can be produced. This loss of material can put at risk
53 both the historic-artistic value of the affected monument and in extreme cases structural
54 problems, which can endanger the stability of the infrastructure and therefore the safety
55 of the people that are inside or around the building.

56 The mobilization and subsequent crystallization of salts, on the surface or within a
57 porous material, is conditioned, among others factors such as pore structure of the
58 material, microclimatic variations and nature of salts, by the following ones: movement
59 of the moisture flow towards the evaporation surface and also by the continuity of this
60 flow inside the material. This continuity depends on the balance between the drying rate
61 of the material, through the evaporation surface, and the water absorption rate by
62 capillary suction [3,7–11]. As long as the continuity in the moisture flow is not lost, the
63 moisture tends to move towards the evaporation surface by advection processes [8]. The
64 direction and sense of these advective processes in monuments where there are different
65 types of construction materials occur towards those materials with the greatest pore
66 volume in the capillary pore range (0.1-100 μm [12]) and within this range, a greater
67 pore volume with a small access diameter. This explains why generally in joint mortars
68 a greater accumulation of salts than in adjacent masonry blocks (either ornamental rocks
69 or bricks) occurs.

Due to this frequent accumulation of salts, decay of mortar is higher than the blocks it bonds, and therefore the mortar is one of the most renewed material in historic masonries [13,14]. Cultural heritage conservation field has investigated the use of different repair mortars, to recover the integrity and continuity of the façade reducing the voids and discontinuities of its surface, and in consequence, hindering the entry of external agents that can promote weathering processes.

Currently and due to the difficulty - sometimes impossibility - of acting on the source of salts, one of the most used strategy to mitigate the damage caused by them consists on reducing its content within the affected material by the application of different desalination techniques, such as: immersion baths [15,16] (only valid for small elements), application of sacrificial mortars and poultices [17–20] (not suitable for historic or artistic finishing), electrokinetic techniques [21–25] and the use of crystallization modifiers [26–28]. Most of these desalination techniques can be considered as shock treatments, i.e., treatments that during their application reduce the ion content in the material, although once the treatment is finished its effect disappears, and the re-entry of the salts can take place again. For this reason, there is a current mainstream in conservation science about the development and application of preventive techniques [29,30].

With the aim of improving the protection of construction materials against the action of soluble salts, especially for built cultural heritage, this study proposes assessing under laboratory conditions the suitability and efficacy of applying repair joint mortars with added modifiers for bonding building materials subjected to salt crystallization processes (similar conditions to those that exist on site), in order to: 1) protect the mortar during the process of curing, hindering the damage caused by salts that may come from the adjacent stone ashlar, 2) favor the entry of the modifier compound into

the weathered surrounded stones in order to remove the salts in the form of efflorescence, and 3) obtain a lasting protective method against salts (specially NaCl) over time. By this way, during the wetting periods of the monument, the releasing of the modifier contained in the mortars can protect both the mortar and the surrounded materials (stone ashlar or bricks).

Recent studies have shown 1) that the use of modifiers can limit or reduce the harmful effects caused by soluble salts, due to:

a) the thermodynamic effect: the modifiers prevent or slow down the salt crystallization, allowing to keep a high concentration inside the pores [31–33]. In consequence, salts remain for a longer time dissolved and can be moved, with the favorable conditions for it, towards the evaporation surface, where they will crystallize in the form of efflorescence rather than subflorescence [34,35].

b) the kinetic effect: the modifiers change the crystal habit, both on the surface and inside the stone, by causing precipitation under conditions other than equilibrium [33,34,36,37].

2) the parameters that have influence on their effectiveness, such as: the modifier concentration [33–36], the pore system of the material (especially pore connectivity) [27,33,34,38], environmental conditions [32,33,36,39], the nature and the complexity of the salts present in the material since for each type of salt there is usually a specific type of inhibitor, for example: urea, cadmium chloride and ferrocyanides for sodium chloride; borax, phosphonates, sodium dodecyl sulfate for sodium sulphate [26,27,32,33,40], and the application method [27]. In addition, the presence of several salts in the medium, even those with the same anion, reduces the effectiveness of the inhibitor in increasing the saturation concentration of those salts that would be susceptible to the inhibitor action [11].

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

120 However, to the authors' knowledge, no specific study focused on analyzing the
121 effectiveness of these compounds on complex structures was found, i.e. ashlar or
122 bricks bonded by a mortar to shape a masonry, nor studies that assess the suitability of
123 adding these compounds to repairing mortars to achieve an effective and lasting
124 **protective method against soluble salts** for the entire masonry and structure. The aim of
125 this study is analyzing those issues by the comparison in terms of **salt extraction ability**,
126 durability and harmful effects of the application of a joint lime repair mortar to bond
127 sandstone blocks contaminated with NaCl, with and without the addition of a
128 ferrocyanide-based compound (potassium ferrocyanide) as modifier in its composition,
129 which is in direct contact with a source of water with different anions in its composition
130 (chlorides, nitrates, and sulfates).

131 132 **2. Materials and methods**

133 **2.1. Stone material: sandstone**

134 Spain is the seventh largest producer of natural stone in the world after China, India,
135 Turkey, Iran, Italy and Brazil, being the sandstone extracted in the province of Burgos
136 the 7% of the Spanish natural production [41].

137 An ashlar of sandstone, namely Dorada Urbion, quarried in Vilviestre del Pinar
138 (Burgos-Spain, Latitude: 41.951024° N and Longitude: 3.078283° W) was used for this
139 study. This sandstone has been widely used in historic and modern constructions and
140 has characteristics that make it sensible to salt induced decay.

141 Thirty four cubic specimens were obtained from the ashlar: 10 of 5 cm side and 24 of 6
142 cm side.

143 The main sandstone's properties were determined using the 5 cm side-cubic specimens,
144 following several European standards and procedures established in previous

researches: water accessible porosity according to [42], capillary porosity and capillary water absorption coefficient following [43,44] respectively. Mercury accessible porosity and pore size distribution were determined, in duplicate, using a Micromeritics Autopore IV9500 porosimeter and fragments of 1 cm³. This porosimeter works with two ranges of working pressure: one of low pressure between 14-200 kPa and another one of high pressure between 0.20-225 MPa, thus allowing the measurement of pores with an access diameter between 360 µm and 3.8 nm.

The 24 cubic specimens of 6 cm side were used to evaluate the salt extraction ability with the joint mortar. Prior to applying the mortar to bond the stone specimens, these were weighed and contaminated with a solution of 20 wt% NaCl. This salt was selected for being one of the most common salts found in porous building materials and responsible very frequently for the decay of built cultural heritage [2,45]. The contamination process, similar to the one used in [46,47], consisted of 5 cycles, each of them of a duration of 4 days: 2 days of capillary absorption, during which the evaporation and subsequent accumulation of salts took place via the lateral and upper faces of the specimens, followed by a drying process of 2 days at laboratory conditions (24±2 °C and 32±4% RH), during which the salts that are still dissolved are distributed inside the material mainly by advective processes during the evaporation of the solution but also by diffusion processes. The specimens were turned over every cycle to achieve a distribution as homogeneous as possible, by placing the opposite face (top face) in contact with the solution. In this way, as shown in previous works and as it could be observed in the specimens at the end of the contamination process, there was not any surface that presents a greater accumulation of saline efflorescence. At the end of the contamination cycles, all the samples were dried in an oven (45°C) until constant mass and weighed again in order to know the weight gain due to the penetration of salts.

2.2. Mortar

Lime-based mortar was selected due to its higher compatibility than cement-based mortar, in terms of mechanical properties [48,49] and source of soluble salts [50,51], with the typical building materials used in monuments (ornamental rocks and bricks). Mortar was elaborated by mixing four-year matured lime putty from PROEISCON Ltd. (74% Ca(OH)_2 and 89 wt% of water content) with standard silicic (90%) sand from CEN Normsand EN 196-1, ranging its grain size from 0.063 to 2 mm, in a volume ratio 1:3, before the incorporation of ultrapure water. This type of water was used in order to avoid introducing salts into the mortar mixture.

Part of the elaborated mortar was kept without any addition, as a reference (onwards MR), and in the other part of the mortar a modifier was added (onwards MM). In this case a 1.23 wt% of potassium ferrocyanide (potassium hexa-cyanoferrate (II) trihydrate from Sigma-Aldrich, $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$) with respect to the binder was added. Ferrocyanide was selected because it is the modifier that provides the highest supersaturation for NaCl nucleation [33,52]. Previous studies have shown that alkaline ferrocyanides allow: 1) to inhibit the crystallization process by delaying the onset of NaCl nucleation, both in mortars [36,37,53,54] and in other porous building materials (limestone [35,55], granite [27,34], sandstone [38] and bricks [32]), 2) to increase the concentration of NaCl leading to the solution supersaturation, and 3) to modify NaCl crystallization habit from cubic to a dendritic one with low adherence to the surface of the material [27,31,32,34,36,55].

The amount of ultrapure water added to the mortar was 15.10 wt% (in MR) and 15.59 wt% (in MM) with respect the mix lime putty and aggregates. This amount was considered enough to achieve an adequate workability and consistency according to the

slump test [56]. The greater water content added to MM than MR was related to the highest concentration of ions in the mortar composition and the necessity to reduce the viscosity in order to achieve a similar workability.

The main physical properties of both mortars (MR and MM) were determined following the same procedures as those used to characterize the sandstone: water and mercury accessible porosity [42], capillary porosity [43], capillary water absorption coefficient [44] and pore size distribution. For this purpose, 8 mortar cubes of 4 cm side, demolded after two days and cured under laboratory conditions (24 ± 2 °C, 32 ± 4 %RH and 678 ± 53 ppm CO₂) during 28 days, were used per kind of mortar (MR and MM), as well as cubic mortar fragments of 1 cm side, extracted both from the mortar cubes and from the joint mortars applied to bond the sandstone samples, were used to analyze, in duplicate, the pore size distribution.

2.3. Experimental setup

Couples of 6 cm side stone specimens contaminated with a solution of 20 wt% NaCl were bonded by a 2 cm thick layer of lime mortar to set up the assembly (Fig. 1a), 6 couples without modifier (onwards S-MR-S) and 6 couples with modifier (onwards S-MM-S). For this purpose, the stone surfaces were pre-wetted before the application of 3 cm of mortar. After that, a light pressure was applied to achieve a good adhesion reducing the thickness of the mortar in 1 cm. Finally, the protruded mortar from the surface of the sandstone blocks was removed. The term S-M-S will be used onwards to refer to both assemblies.

Each of the twelve S-M-S assemblies were left curing under laboratory conditions (24 ± 2 °C, 32 ± 4 %RH and 678 ± 53 ppm CO₂) during 28 days, which was considered enough to achieve a sufficient setting to be able to carry out the experiments. Every 5

days all the assemblies were weighed. During this curing process, the S-M-S assemblies were placed with the mortar joint horizontally to favor the bonding between both stone specimens (see Fig. 1a).

The efflorescence formed on the surface of the assemblies after the 28 days of curing was collected by brush or scalpel, depending on the case, and weighed. After that, four S-M-S (2 of S-MR-S and 2 of S-MM-S assemblies) were used to analyze the initial distribution of chloride in the bulk of both stones and mortars. For this purpose, each of the sandstone specimens was divided by hammer and chisel into 8 equal parts, and the joint mortar layer samples into two parts (see Fig. 1). Each of these parts was weighed and powdered. From each of the sandstone and mortar powder obtained, two samples of 0.15 g were taken and stirred by ultrasound waves in 15 mL of ultrapure water during 45 min. After filtration through 0.45 μm opening mesh sieve, the chloride content was analyzed by high resolution chromatography - IC - (Metrohm 761 Compact IC). With the data gathered by IC and making an average between the chloride content present in the rock parts that are at the same height (for example: average between the parts 1 and 2), the distribution of chloride throughout the assembly was determined, in 2D, using a mathematical software (Surfer 8.0) and using kriging process as statistical interpolation method.

The other eight S-M-S (4 of S-MR-S and 4 of S-MM-S assemblies) were used to analyze the effectiveness of the mortar as a protective method against the crystallization of salts as subflorescence. For this purpose, the S-M-S assemblies were dried to constant weight and after that were placed, with the mortar joint in a vertical arrangement, in plastic containers of 1.5 L capacity (Fig. 1b). Inside each container there are two supports on which the assemblies were placed. The volume of each container from its base to the top of the supports is 1 L, so only 0.5 L can be absorbed

by the assembly during the **wetting** process by capillarity. Once the assembly was placed in the container (onwards system: S-M-S + C) its weight was again recorded, both before and after pouring 1.5 L of tap water into the container, which composition is, in mg/L: Cl⁻ 11.757, SO₄²⁻ 8.378 and NO₃⁻ 1.038. The system was then sealed, on the water surface, with adhesive plastic film to force the evaporation only through the S-M-S assembly, recording its weight once more (starting point of the test). **This procedure to measure the evaporation rate of solutions through the stony materials is similar to that used in previous studies [34,35].**

This test, made under the same laboratory conditions as stated before, simulates the penetration of water by capillarity into the building materials that constitute a wall, either through the ground or through other previously saturated materials, while evaporation takes place on its surface.

INSERT FIGURE 1

2.4. Assessment of the **protective effectiveness, durability and harmful effects of the method **during a wetting phase****

In order to assess how the addition of modifiers in the mortar composition allow to **force the migration of salts presents within** the surrounding stones and increase the salt crystallization resistance of the mortar, the following determinations were performed:

- Water evaporation rate during the **wetting phase**. Each system (S-M-S + C) was weighed daily until the evaporation of the 0.5 L of water or until constant weight was reached. Besides, a photographic record was obtained to visualize the damage of both mortars and stone, and to get the distribution and morphology of the efflorescence on the surfaces.

- At the end of the wetting phase, before removing each assembly S-M-S from the containers, all the formed efflorescence was collected from the surface by brush or scalpel and weighed. These measurements, together with the comparison between the S-M-S dry weight before and after the wetting process, allowed assessing the ratio between efflorescence and subflorescence (Eqs. from 1 to 4).

$$\text{Subflorescence (g)} = \text{S-M-S}_{\text{initial dry weight}} - \text{S-M-S}_{\text{final dry weight}} \quad [\text{Eq. 1}]$$

$$\text{Total salt content (g)} = \text{Efflorescence} + \text{Subflorescence} \quad [\text{Eq. 2}]$$

$$\text{Efflorescence (\%)} = 100 \cdot \text{Efflorescence (g)} / \text{Total salt content (g)} \quad [\text{Eq. 3}]$$

$$\text{Subflorescence (\%)} = 100 \cdot \text{Subflorescence (g)} / \text{Total salt content (g)} \quad [\text{Eq. 4}]$$

This ratio was also determined, as a verification method, by comparing the weight of the efflorescence collected with respect to the subflorescence that remained in the entire assembly calculated from the IC measurements.

- The ability to force the salt migration was evaluated at different times of the wetting phase, establishing as the starting point of each assembly the initial distribution of the existing salts in their respective assembly (S-MR-S and S-MM-S). The first wetting step was stopped after two weeks (2 S-M-S per assembly), while the second wetting step (another 2 S-M-S per assembly) were extended for 11 days long. In both cases, these time intervals were determined by the evaporation of the 0.5L of water. The final content and distribution of the salts in each of the assemblies was determined following the analytical procedure described above in section 2.3.

At the end of each test, the height of the water remaining inside the container was determined, as well as its volume and the chloride content (by IC) that was mobilized towards the water by diffusion, due to the expected existence of a concentration gradient between the assembly and the tap water. Stone and mortars fragments were used to analyze: 1) the morphology of the formed NaCl crystals, both inside and on the

material's surface, by Scanning Electron Microscopy using a Jeol JSM-6330F microscope. Energy dispersive X-ray analysis (EDS) coupled to the microscope, was used in order to perform elemental analysis of the mortar, before and after the wetting process. 2) Modifier content that remains in the mortar at different phases of the treatment by X-ray fluorescence (XRF) using a non-destructive Niton Serie XL3t equipment from Thermo Scientific. A total of 5 measurements, per phase of treatment and mortar, were taken in order to increase the accuracy.

For the evaluation of harmful effects associated to the use of this inhibitor in the mortar composition as a protective technique, the following two parameters were determined:

1) Color changes, both on the mortars' and stones' surface, and also the risk of intervention, since previous studies indicate that the presence of a high concentration of ferrocyanides in a porous material can trigger color changes that discourage their use [27,35]. For this purpose, before and after each test (15 days after drying at room conditions), chromatic parameters of each S-M-S assembly, both the surface of mortars and sandstone specimens, were measured using a Minolta CM-700d spectrophotometer. A total of 20 random measurements per sandstone specimen and mortar were recorded. Color was expressed in the CIEL* a^* b^* color space. The measurements were taken including the specular component (SCI mode), spot diameter of 8 mm, illuminant D65 and an observer angle of 10°. Color differences (ΔL^* , Δa^* , Δb^* , ΔC^*_{ab}) and total color difference (ΔE^*_{ab}) caused in each material were calculated, taking the initial color as the reference value.

2) Carbonation degree of both mortars applied between salt laden sandstones, at different times of the test (after 28 days of curing and at the end of the two wetting phases). For this purpose, thermogravimetric analysis with simultaneous differential scanning calorimetry (TG-DSC) were performed using a SDT-Q600-DSC Q-200, in N₂

atmosphere 10°C/min heating rate. Two dried and grinded mortar samples (10 mg each one) obtained from the different assemblies tested were used. Also two samples were obtained from mortar cubes after 28 days of curing. The carbonation degree was calculated from the relation between portlandite (Ca(OH)_2) depletion and calcite formation (CaCO_3) since the initial values were measured on dried lime putty.

3) Integrity of the mortar. This parameter was evaluated macroscopically, analyzing daily its consistency visually.

3. Results and discussion

3.1. Sandstone characterization

Dorada Urbion is a subarkose, a medium grained sandstone with uniform texture mainly composed of quartz (65%) feldspars (30%) and rock fragments (10%), with a moderately well-sorted sediment [41]. Under a geological point of view, it belongs to the Urbion geological group, and to the fluvial Weald Facies (Cameross Mountain Range). It presents a light beige tone with ochre streaks due to the presence in its composition of iron oxy-hydroxides.

Regarding the main physical properties, related to the porosity properties, of this sandstone (Table 1), it can be noticed that: 1) this stone has a high accessible porosity to water, which makes it a rock highly susceptible to salt damage; 2) the difference between the values of the porosity accessible to water and to mercury (approximately 4%), and that the accessible to water was less than that to mercury, indicates that this stone has a certain pore volume below a pore size diameter of 0.1 μm , which correspond to pores not accessible to water, and 3) the difference between water accessible porosity and capillary porosity (approximately 4%) indicates that part of the sandstone's pore volume do not lies within the capillary range between 0.1-100 μm [12].

345
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

346 INSERT TABLE 1

347
348 With respect to the pore size distribution (see Fig. 2), the sandstone shows a tri-modal
349 pore size distribution: 1) a pore range lower than 0.1 μm (peaking at 0.01 μm), 2)
350 another range between 0.1-1 μm (peaking at 0.1 μm), 3) and a range of pores between
351 1-3 μm (peaking at 1 μm). About 57 % of the total pore volume lies within the range
352 between 0.1-1 μm and the 78% lies within the capillary range between 0.1-100 μm (see
353 Table 2). Only 20% of the total porosity lies in the nanometer range.

354
355 INSERT FIGURE 2

356 INSERT TABLE 2

357 358 **3.2. Mortars characterization**

359 Table 1 shows the data of the main physical properties, related to porosity, of both
360 mortars used in this study (MR and MM).

361 In general, it can be noted that: 1) the accessible porosities, both to water and to
362 mercury, and capillary porosity of both mortars are higher than for sandstone. This
363 higher capacity of capillary absorption of both mortars explains why during the wetting
364 process the water rising occurs preferentially from the mortar, passing later on to the
365 stone specimens, where the dissolution of salts takes place. During the drying process,
366 the preferential evaporation front is the mortar itself, producing a return of the water
367 flow and an accumulation of salts inside it, process similar to the one that governs the
368 operation of the poultices [58,59]. 2) The fact that accessible porosity to water, in both
369 mortars, is higher than the mercury accessible porosity indicates that in both mortars,

but especially in the MM one, there is a certain pore volume with a size diameter higher than the measuring range of the porosimeter (360 μm). This fact is related with the range of pores that plays an important role in each porosity: pores accessible to water are those with an access diameter greater than 0.1 μm , and pores accessible to mercury are those with an access diameter between 0.00387-360 μm .

Comparatively, the presence of the modifier in the mortar composition causes a slight increase in the water accessible porosity (an increase which, **considering** the deviation, is not statistically significant). However, with respect to the mercury accessible porosity, the results are opposite, i.e. this parameter is higher in MR than in MM. This may be related to the existence of a larger pore volume not accessible to water (pores below 0.1 μm) in MR and also, as mentioned above, with the existence in MM of a greater pore volume with an access diameter higher than 360 μm in this mortar.

Regarding the pore size distribution and the volume of mercury intruded at different intervals of pore access diameter (see Fig. 2 and Table 2, respectively), it can be seen that both mortars have a similar pore size distribution with two main families: one between 0.1-1 (peaking at 0.2 μm) and another range between 10-100 (peaking at 20 μm). Slight differences can be observed when analyzing the volume intruded by pore range: MR shows a higher pore volume in the range between 0.1-100 μm , which explains why the capillary porosity is higher in this mortar than in MM.

3.3. Water evaporation rate and efflorescence/subflorescence ratio

3.3.1. During curing process

Figure 3 shows the average weight loss rate of water, of each type of assembly, during the curing process. This weight loss rate was greater and faster when MM was applied between the sandstone specimens, increasing the difference as the curing process

progressed. This different behavior between mortars is related to water evaporation and also to the release of part of the salts present in the S-M-S assemblies.

INSERT FIGURE 3

In the S-MR-S assemblies, the water supplied by the mortar penetrated into the sandstones producing a dissolution and subsequent mobilization of the salts during the drying process. During this lapse of time the formation of efflorescence on the surface of any of the stone specimens and on the mortar too, was almost negligible (see pictures Figure 3), only the slight whitish color observed in some areas indicates the presence of a few quantities of salts.

In the S-MM-S assemblies the behavior was different. The entry of the moisture front into the stones, with modifier, allowed dissolving part of the salts (as occurs in the S-MR-S assembly) and moving them towards the evaporation surface, where they precipitated in the form of efflorescence (approximately 2.65 g to 0.5 cm from the contact zone sandstone-mortar and a few quantities on the mortar). This is due to: 1) the potassium ferrocyanide acts as a strong nucleation inhibitor of NaCl, delaying the onset of crystallization, as occurs in [27,31,33,36]. 2) the presence of ferrocyanide causes changes on the NaCl crystal morphology, favoring the formation of dendritic efflorescence, which acts as a porous network that increases the effective surface area for evaporation (creeping process [31,35,38,55,60]).

As a result, at the end of the curing process it was observed that in sandstone samples bonded by MM, approximately 25% of the salts crystallized on the surface of the stone as efflorescence, while in the sandstone samples bonded by MR, 98% of the salts

continued as **subflorescence** (see Table 3). This fact leads to less damage risk to the S-MM-S assembly than the S-MR-S due to its lower content of **subflorescence**.

INSERT TABLE 3

3.3.2. During the wetting process

The trend shown during the **wetting process** was similar to that observed previously during the 28 days of curing. During the **wetting process** (see Fig. 4) the weight loss was greater and faster in the S-MM-S assemblies than in the S-MR-S ones, due to the action exerted by the ferrocyanide on the nucleation of NaCl and to the change of habit of crystallization of the chloride on the surface, both aspects favoring the greater evaporation of the assembly.

INSERT FIGURE 4

During the first **wetting phase** the behavior shown by both assemblies was different: 1) From the beginning of the **wetting process**, a release and subsequent chloride crystallization was observed in all the assemblies (see Figure 5). However, the salt adhesion and crystallization habit formed on the surface of both materials (stone and mortar) was different. In the S-MR-S assemblies, NaCl crystallized forming a compact crust strongly adhered to the stone and mortar surfaces, blocking the superficial pores. While in the S-MM-S assemblies, NaCl crystallized forming dendritic efflorescence, slightly adhered to the assembly surface, which did not block the stone and mortar pores (see Fig.6). This different habit of crystallization has an influence on the evaporation dynamics of the material and also on its resistance against the damage caused by salts.

Surface salt crust, as other studies point out [36,38], reduces the evaporation rate of sandstone favoring the future salt precipitation some millimeters beneath the surface, i.e. inside the material, which increases the damage caused by salts. On the contrary, dendritic efflorescence increases the evaporation flux pumping more dissolve salt ions towards the surface [27,31,34,38].

INSERT FIGURE 5

2) After two days of treatment (approximately 3000 min), a fracture, in the S-MR-S assemblies, caused the loss of adhesion between the mortar and one of the sandstone specimens. Probably the crystallization pressure exerted by NaCl salts favored this bond loss between the mortar and substrate. Similar problem to that one usually happens in monuments where, as stated in [61], the interface between both materials with different physical, chemical and electrochemical properties is usually a weak zone prone to be damaged by different alteration mechanisms. This fracture process and subsequent loss of adhesion did not occur in the S-MM-S assemblies because the salt output, as dendritic efflorescence, reduced the pressure that they can exert inside the mortar's pores.

Despite this loss of adhesion, weight was continuously recorded in the S-MR-S assemblies until the **first wetting phase** was considered finished in the S-MM-S assemblies (this moment occurred after 14 days of treatment, when it was observed that the S-MM-S assemblies absorbed the 0.5 L water with which they were in contact). During this time it was shown, especially in the S-MM-S assemblies, that their integrity was not lost, as the wetting front was advancing from the vicinity of the mortar towards

the corners of the sandstone specimens, favoring the removal of the salts and its subsequent crystallization on the surface (see Figure 5).

INSERT FIGURE 6

During the second **wetting phase**, the weight loss of water recorded in the S-MM-S assembly was higher than that recorded in the S-MR-S one, similar result to that recorded during the first step (see Fig. 4). However, during this step hardly any efflorescence was generated on the S-MM-S assembly, which could indicate that inside this assembly there is hardly any chloride.

Consequently, the result recorded during this second step cannot be assigned to the higher evaporation caused by the dendritic efflorescence. This result seems to be related to 1) the blockage of the surface pores, both in stones and mortar, and therefore to the reduction of evaporation capacity of the assembly. The absorption of water of the S-MR-S assembly during the entire **wetting** process was very low (approximately 0.2 L per step), due to the fact that the evaporation process was hampered by the surface salt crust. However, the S-MM-S assembly could absorb, in both **wetting phases**, the 0.5 L water with which it was in contact, thanks to the fact that the evaporation capacity of the assembly was not limited and 2) a probable reduction in the solution-stone contact angle, as occurs in [26,27], which could improve capillary transport.

Regarding the distribution of the salts (see Table 3), it was observed that in the S-MR-S assemblies and after the first **wetting phase**, around 70% of salts formed a hard and compact surface crust, remaining 30% of the salts as **subflorescence**. Both percentages changed after the second **wetting phase**, an increase in the content of salts that crystallized at the surface was noted (75% efflorescence and 25% **subflorescence**).

During the removal of the salt crust, part of the surface of the sandstone was detached. There were also signs of alteration by salts at the corners of the sandstone specimens bonded by MR. In the S-MM-S assemblies, the difference between the amount of efflorescence with respect to **subflorescence** was much higher (99% approximately) than for S-MR-S assemblies. Furthermore, the distribution of chloride in the sandstone specimens hardly varied between the two **wetting phases**, which could indicate that the salt extraction process after the first **wetting phase** was already high. In any case, this result indicates that the use of mortars with potassium ferrocyanide allows reducing the risk of damage that a material may suffer by the action of sodium chloride.

3.4. Salt migration

3.4.1. During curing process

Figure 7 shows the chloride distribution (in mg) in the S-M-S assemblies at different moments of the study (curing phase, and first and second **wetting phases**).

In general, it can be noticed that the amount and distribution of the salts during the curing process was different depending on when the sandstone specimens were bonded by MR or MM.

In the S-MR-S assemblies, a greater concentration of chloride was observed both inside the mortar (1000 mg) and in the sandstone surface that was in contact with it (800 mg). This distribution is related to the dissolution of part of the salts during the phase of penetration of water from the mortar into the sandstone (see Figure 5), and the subsequent mobilization of the salts towards the mortar by advection, i.e. during the evaporation phase, due to the greater capillary suction of mortar than sandstone (see Table 2).

On the other hand, in the S-MM-S assemblies, 1) a lower concentration of chloride than in the S-MR-S assemblies was measured, especially inside the mortar and in adjacent areas of the stone. This is due to the release of part of the salts outwards in the form of efflorescence, and 2) the mobilization of chloride towards the mortar during the evaporation of water was lower than for S-MR-S assemblies. This is because the capillary suction force exerted by the mortar was partially offset by that exerted by the saline efflorescence formed both on the surrounding sandstone surfaces, and even on the mortar surface. This efflorescence, as stated in [31,60,62], and as it was observed in figure 3, allows increasing the evaporation surface of the assembly, and in consequence, pumping more dissolve salts towards its surface (creeping process [60]).

INSERT FIGURE 7

3.4.2. During the wetting process

During the wetting process, in general, the initial ion content was reduced in both assemblies (see Fig. 7), without a significant increase in the effectiveness of the process over time, i.e. between the end of the first and the second wetting phases.

However, the following differences between both assemblies were notices:

1) The effectiveness to force the chloride migration towards the surface was higher in S-MM-S than in S-MR-S assemblies. The results of IC analysis in S-MM-S assemblies at different times of the treatment, as well as the visual control of the assemblies, showed how the advance of the ferrocyanide during the wetting process allowed to "sweep", by advection, the chloride content throughout the assembly (see Figure 5), reducing the chloride content after the first wetting phase to concentrations close to 0 mg. This reduction was similar to that achieved after the second wetting phase.

In the S-MR-S assemblies the final chloride content, after the first wetting phase, was very far from that detected in S-MM-S assemblies, around 100 mg in the mortar and higher in the stone areas further away from the mortar (between 240-300 mg). After the second wetting phase, the highest accumulation of chloride was observed in the assemblies' superficial zones (between 200-380 mg), just in the fringe below the salt crust that was removed before the analytical process by IC, and the lowest to the assemblies' bottom zones that were close to the water (between 20 and 150 mg).

2) The predominant mobilization mechanism of salts was different in each assembly. In both assemblies salts were mobilized by advection towards their evaporation surfaces, and by diffusion towards the water present in the container. This last one, was higher in S-MR-S than in S-MM-S assemblies (between 3.17-4.06 g and 1.39-2.11 g, respectively), and by advection towards the surface it resulted the opposite, i.e. higher in S-MM-S assemblies. The reason for this different mobilization is related to a decrease in the evaporation process due to the formation of the superficial crust that clogs these pores, promoting an accumulation of chloride beneath the surface, and leaving as a preferential exit the diffusion of salts towards the humidity source with which the assembly is in contact. On the contrary, as commented in section 3.3.2, efflorescence improves the evaporation of the assembly favoring the release of salts by advection.

The high ability to force the migration of chloride outside the sandstone specimens by using MM allowed to reduce the chloride content to such low levels that the accessible porosity to mercury of this stone at the end of the test (16.19%) was very close to the initial one (18.89%), while with the use of MR, the presence of salts caused that the value of this porosity at the end of the treatment was much lower (12.60%).

3.5. Salt crystal morphology and modifier content

Figures 8 and 9 show SEM micrographs of MR, MM and sandstone specimens, respectively, in the contact surface between both materials and also cross section, at the end of the wetting process.

In general it can be noticed that both inside and on the surface of both materials (mortars: MR and MM and sandstone specimens), the habit of crystallization was different depending on the presence or absence of the modifier. This result is consistent with those obtained in previous studies [34,36,37,55].

In MR and in sandstone specimens in contact with this mortar, the sodium chloride crystallized with a cubic shape, typical of the halite, or form a compact salt crust. However, in the presence of the potassium ferrocyanide a change in the habit of crystallization of sodium chloride, both inside the MM mortar and in the sandstone, occurs forming elongated prisms of smaller size or filaments. This reduction in the size of the crystals, as indicate [38], facilitates the mobilization of the salts through the pores and reduce the damage caused by the possible crystallization pressures.

INSERT FIGURES 8 AND 9

Regarding the modifier content that remains in MM, a decrease was observed between the curing process and the first wetting phase of the treatment (from a Fe content of 980 ± 80 ppm to 800 ± 70 ppm) during which the highest removal rate of salts was achieved. However, this content scantily varied when increasing the wetting time (from 800 ± 70 ppm to 820 ± 70 ppm). This indicates that the amount of modifier that remains in the mortar is sufficient to protect, against chloride crystallization, the adjacent area if this salt come back inside. This method seems to be not only a shock treatment against salt damage but can also be considered as a preventive treatment.

3.6. Harmful effects: color changes, carbonation degree and integrity

Regarding sandstone specimens, the color changes after the contamination process with NaCl were mainly caused by changes in the L^* coordinate due to the entry of salts (see Table 4, 1). After the wetting process (2) the changes in luminosity were higher in the stone specimens in contact with MM, while in the chroma C^* in the samples bonded by the MR. The total global color change (ΔE^*_{ab}) recorded after the wetting process in the intervention carried out using MR exceeded the value of 5, higher than that using MM. These changes are related to the salt crust that remains on the surface of the rock in the samples joined by MR and to the whitish color that remained in the samples joined with MM when the salts come out.

Regarding mortars, the color changes caused by the entry of salts from the stone specimens during the curing process (1) were qualitatively similar. However, quantitatively the color changes with MM were caused mainly by changes in the luminosity L^* while with MR, by changes in the chroma C^* .

After the wetting process (2) using MR, ΔE^* change on the surface of the mortar was higher than 5, caused mainly by the formation of the salt crust on the mortar surface. However, by using MM, the high removal rate of salts outside the mortar allowed to recover its original color.

In any case, no stains were observed on the surface of both materials, as it happened in other previous studies [27,35], noticing that the use of MM tends to return the original color of both mortar and stone due to the high salt removal rate. The reason of why no stains have been observed is related to the leaching rate of the ferrocyanide and to its very low concentration that will penetrate in the surrounded stones, which will be lower than that in the mortar.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

618
619 INSERT TABLE 4
620

621 In the TGA-DSC analysis, the used lime putty had 70.9 % weight loss associated to
622 portlandite dehydration and 16.4% weight loss associated to calcite decomposition.
623 Regarding mortar carbonation degree, it was observed that 1) After the curing process
624 (28 days) a higher degree was observed when the inhibitor was added to the mortar,
625 both in the mortar cubes (MR:28.5% and MM:41.0%) and also when the mortar was
626 applied between salt-laden sandstones (MR:43.3% and MM:48.5%). This increase
627 caused by the use of ferrocyanide, after 28 days, was observed also in [53, 54]. This
628 improvement in the carbonation degree (30% more in cubes and 12% between salt laden
629 blocks when ferrocyanide was added to the mortar) seems to be related mainly to the
630 faster drying rate that occurs when inhibitor is used. As stated in [63,64], the faster
631 drying rate of a material and the lower its water content, the greater the rate of CO₂
632 diffusion coefficient required for carbonation (in air is $1390 \cdot 10^{-8} \text{ m}^2\text{s}^{-1}$ while in water is
633 $10^4\text{-}10^5$ times less). This fact explains also the higher carbonation degree achieved in the
634 mortars located between sandstone blocks than that achieved in mortar cubes, since the
635 suction of part of the water by the stones favor the distribution and diffusion of
636 atmospheric CO₂.
637 Taking into account these data, in which a greater degree of carbonation achieved in
638 MM mortars was appreciated and also that the greater carbonation degree, the greater
639 weight increase of the mortar [65], it can be assumed that the difference recorded in the
640 water evaporation curves between the two mortars is higher than that recorded (see Fig.
641 3). This fact once again shows the increase in the evaporation capacity of water
642 produced in the mortar when the ferrocyanide is added.

At the end of the wetting process (after 25 days more in which the assemblies were partial immersed in water) the carbonation degree was 40% and 32% in MM and MR, respectively, i.e. a reduction in the carbonation degree was observed in both mortars, but this degree continued to be greater in the mortar MM. This reduction in the carbonation degree could be attributed to the re-precipitation of calcium hydroxide triggered by the dissolution of possible hydration reaction products and most likely to the precipitation of less stable calcium carbonates. The highest carbonation degree reached in the presence of ferrocyanide could be related with the highest open porosity and permeability of MM mortar (factor that have influence in the carbonation degree [66]), and also with the amount of salts present in the mortars, which can occlude some pores and hinder the diffusion of CO₂. The saline phases were not clearly detected due to the probable juxtaposition of the phases in the mortars; however, the re-carbonation peaks due to the salts presence was obvious in MR after the wetting process. More information is given in [54].

Finally, with respect to the mortar integrity, it was observed that during the whole test (curing and wetting processes), and after disassembled the SMS assemblies, the MM mortar showed a good integrity, without signs of rupture or damages, while MR showed a minor integrity decomposing just by touching it which may be due to: 1) the higher content of salts inside, which caused de-cohesion between the binder and aggregates, and detachment, and 2) the lower degree of carbonation reached that may influence in the mortar strength.

4. CONCLUSIONS

The main conclusions that are drawn from this study are:

- Mortars with ferrocyanide are suitable to be used as repairing ones, and also as a protective technique against salt crystallization when the chloride is the main anion that contaminates the stone.
- The ferrocyanide protects the mortar during the curing process expelling the chloride that is nearby and increasing its carbonation degree.
- The ferrocyanide allows reaching a good adhesion between mortar and stones contaminated with sodium chloride, due to the ability to hinder the entry of this salt inside the mortar, and also due to the possibility of force their migration towards the surface of the surrounding stones.
- The use of ferrocyanides promotes the formation of non-destructive chloride efflorescence rather than destructive subflorescence on the surrounding materials, decreasing the amount of chloride crystallized inside them.
- A low concentration of modifier is sufficient to protect against chloride crystallization the adjacent stones for a long period of time without causing aesthetic changes, both in the stones and in the mortar.

Rarely modern buildings and monuments are contaminated with single salts, for this reason and as a future research line it would be interesting to study the behavior of some modifiers against mixed salt systems commonly present in buildings.

Funding

This research was funded by the CLIMORTEC Project (BIA2014-53911-R) of Ministry of Economy and Competitiveness of Spain, and the TOP Heritage program (P2018/NMT-4372) of the Community of Madrid. J. Feijoo's work is supported by the

Ministerio de Ciencia Innovación y Universidades, Spanish Government, through a Juan de la Cierva grant.

Acknowledgments

Special acknowledgments to the professional support of the Interdisciplinary Thematic Platform from CSIC *Open Heritage: Research and Society (PTI-PAIS)* and to Blanca Gallardo for her hard work at the time of performing IC analysis.

Authors' contributions

Jorge Feijoo: Conceptualization, Methodology, Formal analysis, Investigation, Writing-Original Draft, Supervision **Duygu Ergenç:** Formal analysis, Investigation, Writing-Original Draft **Rafael Fort:** Resources, Writing-Original Draft, Project administration, Funding acquisition **Mónica Alvarez de Buergo:** Writing-Original Draft.

Conflicts of interest/Competing 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.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

REFERENCES

[1] A.E. Charola, Salts in the Deterioration of Porous Materials: An Overview, J.

- 716 Am. Inst. Conserv. 39 (2000) 327-343. doi:10.2307/3179977.
- 717 [2] C. Rodriguez-Navarro, E. Doehne, Salt weathering: influence of evaporation rate,
 718 supersaturation and crystallization pattern, Earth Surf. Process. Landforms. 24
 719 (1999) 191–209. doi:10.1002/(SICI)1096-9837(199903)24:3<191::AID-
 720 ESP942>3.0.CO;2-G.
- 721 [3] R.M. Espinosa-Marzal, G.W. Scherer, Advances in understanding damage by salt
 722 crystallization., Acc. Chem. Res. 43 (2010) 897–905. doi:10.1021/ar9002224.
- 723 [4] A.S. Goudie, H. Viles, Weathering hazards, in: Geomorphol. Hazards Disaster
 724 Prev., (2010). doi:10.1017/CBO9780511807527.012.
- 725 [5] G.W. Scherer, R. Flatt, G. Wheeler, Materials science research for the
 726 conservation of sculpture and monuments, MRS Bull. 26 (2001) 44-50.
 727 doi:10.1557/mrs2001.18.
- 728 [6] ICOMOS International Scientific Committee for Stone (ISCS), ICOMOS-ISCS:
 729 Illustrated glossary on stone deterioration patterns, 2008.
 730 doi:10.3109/14767058.2010.497569.
- 731 [7] R.M. Espinosa-Marzal, G.W. Scherer, Mechanisms of damage by salt, Geol. Soc.
 732 London, Spec. Publ. 331 (2010) 61-77. doi:10.1144/sp331.5.
- 733 [8] L. Pel, H. Huinink, K. Kopinga, Salt transport and crystallization in porous
 734 building materials, in: Magn. Reson. Imaging, 21 (2003) 317-320.
 735 doi:10.1016/S0730-725X(03)00161-9.
- 736 [9] C. Hall, W.D. Hoff, Rising damp: Capillary rise dynamics in walls, Proc. R. Soc.
 737 A Math. Phys. Eng. Sci. 463 (2007) 1871-1884. doi:10.1098/rspa.2007.1855.
- 738 [10] M. Nokken, Water transport in brick, stone and concrete, Cement, Concrete and
 739 Aggregates 25 (2009). doi:10.1520/CCA10518J.
- 740 [11] S. Gupta, Sodium chloride crystallization in drying porous media: influence of

- inhibitor, PhD Thesis, Eindhoven University of Technology, (2013).
- [12] B. Meng, Calculation of moisture transport coefficients on the basis of relevant pore structure parameters, *Mater. Struct.* 27 (1994) 125–134. doi:10.1007/BF02473025.
- [13] V. Corinaldesi, Environmentally-friendly bedding mortars for repair of historical buildings, *Constr. Build. Mater.* 35 (2012) 778-784. doi:10.1016/j.conbuildmat.2012.04.131.
- [14] B. Szemerey-Kiss, Á. Török, The effects of the different curing conditions and the role of added aggregate in the strength of repair mortars, *Environ. Earth Sci.* 76 (2017). doi:10.1007/s12665-017-6597-6.
- [15] S.P. Koob, W.Y. Ng, The Desalination of Ceramics Using a Semi-Automated Continuous Washing Station, *Stud. Conserv.* 45 (2000) 265-273. doi:10.2307/1506863.
- [16] J. Unruh, A Revised Endpoint for Ceramics Desalination at the Archaeological Site of Gordion, Turkey, *Stud. Conserv.* 46 (2001) 81-92. doi:10.2307/1506839.
- [17] N. Husillos-Rodríguez, P.M. Carmona-Quiroga, S. Martínez-Ramírez, M.T. Blanco-Varela, R. Fort, Sacrificial mortars for surface desalination, *Constr. Build. Mater.* 173 (2018) 452-460. doi:10.1016/j.conbuildmat.2018.04.029.
- [18] J. Setina, L. Krage, J. Svare, S. Kirilova, Simulation of desalination processes using lime-based mortars, *Materials Science* 1 (2009) 30–35.
- [19] V. Vergès-Belmin, H. Siedel, Desalination of Masonries and Monumental Sculptures by Poulticing: A Review, *Restor. Build. Monum. an Int. J. = Bauinstandsetz. Und Baudenkmalpfl. Eine Int. Zeitschrift.* 11 (2005) 391-408. doi:10.1515/rbm-2005-6000.
- [20] M.A. Vicente, S. Vicente-tavera, Clay poultices in salt extraction from

- ornamental stones: a statistical approach, *Clays and Clay Minerals* 49 (2001) 227–235. doi.org/10.1346/CCMN.2001.0490305.
- [21] J. Feijoo, X.R. Nóvoa, T. Rivas, M.J. Mosquera, J. Taboada, C. Montojo, F. Carrera, Granite desalination using electromigration. Influence of type of granite and saline contaminant, *J. Cult. Herit.* 14 (2013) 365–376. doi:10.1016/j.culher.2012.09.004.
- [22] J. Feijoo, L.M. Ottosen, J.S. Pozo-Antonio, Influence of the properties of granite and sandstone in the desalination process by electrokinetic technique, *Electrochim. Acta.* 181 (2015) 280–287. doi:10.1016/j.electacta.2015.06.006.
- [23] J. Feijoo, O. Matyščík, L.M. Ottosen, T. Rivas, X.R. Nóvoa, Electrokinetic desalination of protruded areas of stone avoiding the direct contact with electrodes, *Mater. Struct.* 50 (2016) 82. doi:10.1617/s11527-016-0946-x.
- [24] J. Feijoo, L.M. Ottosen, O. Matyscak, R. Fort, Electrokinetic desalination of a farmhouse applying a proton pump approach. First in situ experience, *Constr. Build. Mater.* 243 (2020). doi.org/10.1016/j.conbuildmat.2020.118308.
- [25] J. Feijoo, T. Rivas, X.R. Nóvoa, I. de Rosario, J. Otero, In situ desalination of a granitic column by the electrokinetic method, *Int. J. Archit. Herit.* 12 (2018) 63–74. doi:10.1080/15583058.2017.1370509.
- [26] C. Rodriguez-navarro, E. Doehne, E. Sebastian, Influencing Crystallization Damage in Porous Materials through the Use of Surfactants: Experimental Results Using Sodium Dodecyl Sulfate and Cetyltrimethylammonium Chloride, *Langmuir.* 16 (2000) 947–954. doi.org/10.1021/la990580h.
- [27] T. Rivas, J. Feijoo, I. de Rosario, J. Taboada, Use of Ferrocyanides on Granite Desalination by Immersion and Poultice-Based Methods, *Int. J. Archit. Herit.* 11 (2017) 588–606. doi:10.1080/15583058.2016.1277282.

- [28] C. Rodriguez-Navarro, E. Doehne, E. Sebastian, How does sodium sulfate crystallize? Implications for the decay and testing of building materials, *Cem. Concr. Res.* 30 (2000) 1527-1534. doi:10.1016/S0008-8846(00)00381-1.
- [29] B.H. Wirilander, Preventive Conservation : a Key Method to Ensure Cultural Heritage ' s Authenticity and Integrity in Preservation Process, *Econservation.* (2012) 33-44.
- [30] K. Van Balen, A., Vandesande, Reflections on Preventive Conservation, Maintenance and Monitoring of Monuments and Sites by the PRECOM³OS UNESCO Chair. Leuven/Den Haag: ACCO., (2013) ISBN: 9789033493423.
- [31] S. Gupta, K. Terheiden, L. Pel, A. Sawdy, Influence of ferrocyanide inhibitors on the transport and crystallization processes of sodium chloride in porous building materials, *Cryst. Growth Des.* 12 (2012) 3888-3898. doi:10.1021/cg3002288.
- [32] S. Gupta, H.P. Huinink, L. Pel, K. Kopinga, How Ferrocyanide Influences NaCl Crystallization under Different Humidity Conditions, *Cryst. Growth Des.* 14 (2014) 1591–1599. doi.org/10.1021/cg4015459.
- [33] S.J.C. Granneman, B. Lubelli, R.P.J. van Hees, Mitigating salt damage in building materials by the use of crystallization modifiers – a review and outlook, *J. Cult. Herit.* 40 (2019) 183-194. doi:10.1016/j.culher.2019.05.004.
- [34] T. Rivas, E. Alvarez, M.J. Mosquera, L. Alejano, J. Taboada, Crystallization modifiers applied in granite desalination: The role of the stone pore structure, *Constr. Build. Mater.* 24 (2010) 766–776. doi:10.1016/j.conbuildmat.2009.10.031.
- [35] C. Selwitz, E. Doehne, The evaluation of crystallization modifiers for controlling salt damage to limestone, *J. Cult. Herit.* 3 (2002) 205–216. doi:10.1016/S1296-2074(02)01182-2.

- [36] B. Lubelli, T.G. Nijland, R.P.J. van Hees, A. Hacquebord, Effect of mixed in crystallization inhibitor on resistance of lime–cement mortar against NaCl crystallization, *Constr. Build. Mater.* 24 (2010) 2466–2472. doi:10.1016/j.conbuildmat.2010.06.010.
- [37] S.J.C. Granneman, B. Lubelli, R.P.J. van Hees, Effect of mixed in crystallization modifiers on the resistance of lime mortar against NaCl and Na₂SO₄ crystallization, *Constr. Build. Mater.* 194 (2019) 62–70. doi:10.1016/j.conbuildmat.2018.11.006.
- [38] B. Lubelli, R.P.J. van Hees, Effectiveness of crystallization inhibitors in preventing salt damage in building materials, *J. Cult. Herit.* 8 (2007) 223–234. doi:10.1016/j.culher.2007.06.001.
- [39] S. Gupta, H.P. Huinink, M. Prat, L. Pel, K. Kopinga, Paradoxical drying of a fired-clay brick due to salt crystallization, *Chem. Eng. Sci.* 109 (2014) 204–211. doi:10.1016/j.ces.2014.01.023.
- [40] L. Pastero, D. Aquilano, M. Moret, Selective adsorption/absorption of formamide in NaCl crystals growing from solution, *Cryst. Growth Des.* 12 (2012) 2306–2314. doi:10.1021/cg2015989.
- [41] C. Conde-Vázquez, O. De Miguel-San Martín, G. García-Herbosa, Artificial arenite from wastes of natural sandstone industry, *Mater. Construcción.* 69 (2019). doi:10.3989/mc.2019.12317.
- [42] RILEM (Réunion Internationale des Laboratoires d’Essais et de Recherche sur les Matériaux et les Constructions), Protection et Erosion des Monuments. Recommandations provisoires. Essais recommandés pour mesurer l’altération des pierres et évaluer l’efficacité des méthodes de traitement. Test No. II. 1: Open porosity and Test II. 2: Bulk and real densities., Comm. 25 PEM. (1980).

- [43] A. Bernabeu, E. Expósito, V. Montiel, S. Ordóñez, A. Aldaz, A new electrochemical method for consolidation of porous rocks, *Electrochem. Commun.* 3 (2001) 122-127. doi:10.1016/S1388-2481(01)00117-5.
- [44] ICR-CNR-Instituto Centrale do restauro-Commissione Normal (1985) Doc. NORMAL 11/85. Assorbimentod'acqua per capilarita'. Coefficiente di assorbimentocapillare, (1985).
- [45] B.A. Lubelli, Sodium chloride damage to porous building materials., PhD Thesis, TU Delft, Delft Univ. Technol. (2006).
- [46] J. Feijoo, X.R. Nóvoa, T. Rivas, L.M. Ottosen, Enhancing the efficiency of electrochemical desalination of stones: a proton pump approach, *Mater. Struct. Constr.* 51 (2018). doi:10.1617/s11527-018-1224-x.
- [47] J. Feijoo, T. Rivas, X.R. Nóvoa, L.M. Ottosen, New Double Electrode System for the Electrochemical Desalination of Building Stones, *Int. J. Archit. Herit.* 14 (2020) 678-693. doi:10.1080/15583058.2018.1561962.
- [48] J. Lanas, J.I. Alvarez, Masonry repair lime-based mortars: Factors affecting the mechanical behavior, *Cem. Concr. Res.* 33 (2003) 1867–1876. doi:10.1016/S0008-8846(03)00210-2.
- [49] E.A.W. Hendry, Masonry walls: Materials and construction, *Constr. Build. Mater.* 15 (2001) 323–330. doi:10.1016/S0950-0618(01)00019-8.
- [50] W. Kloppmann, P. Bromblet, J.M. Vallet, V. Vergès-Belmin, O. Rolland, C. Guerrot, C. Gosselin, Building materials as intrinsic sources of sulphate: A hidden face of salt weathering of historical monuments investigated through multi-isotope tracing (B, O, S), *Sci. Total Environ.* 409 (2011) 1658-1669. doi:10.1016/j.scitotenv.2011.01.008.
- [51] B. Silva, B. Prieto, T. Rivas, L. Pereira, Gypsum-induced decay in granite

monuments in Northwestern Spain, *Mater. Constr.* 60 (2010).
doi:10.3989/mc.2010.46808.

[52] V.D.W.I.M. A., Influence of additives on the Growth and Dissolution of Sodium Chloride Crystals, Ph.D. Thesis, Tech. Univ. Twente, Enschede, Netherlands. (1965).

[53] S.J.C. Granneman, B. Lubelli, R.P.J. Van Hees, Characterization of lime mortar additivated with crystallization modifiers, *Int. J. Archit. Herit.* 12 (2018) 849-858. doi:10.1080/15583058.2017.1422570.

[54] D. Ergenç, J. Feijoo, R. Fort, M. Alvarez de Buergo, Effects of potassium ferrocyanide used for desalination on lime composite performances in different curing regimes, *Constr. Build. Mater.* 259 (2020) 120409. doi:10.1016/j.conbuildmat.2020.120409.

[55] C. Rodriguez-Navarro, L. Linares-Fernandez, E. Doehne, E. Sebastian, Effects of ferrocyanide ions on NaCl crystallization in porous stone, *J. Cryst. Growth.* 243 (2002) 503–516. doi:10.1016/S0022-0248(02)01499-9.

[56] AENOR, AENOR: Norma UNE-EN 12350-2:2009, 2009.

[57] J.D. Rodrigues, a. Grossi, Indicators and ratings for the compatibility assessment of conservation actions, *J. Cult. Herit.* 8 (2007) 32–43. doi:10.1016/j.culher.2006.04.007.

[58] L. Pel, A. Sawdy, V. Voronina, Physical principles and efficiency of salt extraction by poulticing, *J. Cult. Herit.* 11 (2010) 59–67. doi:10.1016/j.culher.2009.03.007.

[59] I. de Rosario, J. Feijoo, Alteración de las rocas y otros materiales de construcción en los monumentos. Técnicas de conservación., *Monogr. Da Univ. Vigo. Tecnoloxía* (2016) 294 pages.

- [60] W.J.P. van Enckevort, J.H. Los, On the Creeping of Saturated Salt Solutions, Cryst. Growth Des. 13 (2013) 1838–1848. doi:10.1021/cg301429g.
- [61] M. Sánchez, P. Faria, L. Ferrara, E. Horszczaruk, H.M. Jonkers, A. Kwiecień, J. Mosa, A. Peled, A.S. Pereira, D. Snoeck, M. Stefanidou, T. Stryzewska, B. Zając, External treatments for the preventive repair of existing constructions: A review, Constr. Build. Mater. 193 (2018) pp. 435-452. doi:10.1016/j.conbuildmat.2018.10.173.
- [62] S. Veran-Tissoires, M. Marcoux, M. Prat, Discrete salt crystallization at the surface of a porous medium, Phys. Rev. Lett. 108 (2012) 054502. doi:10.1103/PhysRevLett.108.054502.
- [63] K. Van Balen, D. Van Gemert, Modelling lime mortar carbonation, Mater. Struct. 27 (1994) pp. 393–398. doi:10.1007/BF02473442.
- [64] M. Arandigoyen, J.I. Alvarez, Pore structure and mechanical properties of cement-lime mortars, Cem. Concr. Res. 37 (2007) pp. 767-775. doi:10.1016/j.cemconres.2007.02.023.
- [65] M. Arandigoyen, B. Bicer-Simsir, J.I. Alvarez, D.A. Lange, Variation of microstructure with carbonation in lime and blended pastes, Appl. Surf. Sci. 252 (2006) 7562–7571. doi:10.1016/j.apsusc.2005.09.007.
- [66] L. Ventolà, M. Vendrell, P. Giraldez, Newly-designed traditional lime mortar with a phase change material as an additive, Constr. Build. Mater. 47 (2013) pp 1210-1216. doi:10.1016/j.conbuildmat.2013.05.111.

FIGURE CAPTIONS

Figure 1. Scheme of the assemblies evaluated in this research, with mortars made with and without modifier, during the curing process (assemblies in vertical position: a) and during the **wetting** process (assemblies in horizontal position: b). The division of the sandstone specimens into 8 equal parts and the mortar into 2 is also shown.

Figure 2. Pore size distribution ($n=2$) of the sandstone and the mortar made both with and without crystallization modifiers.

Figure 3. Average weight loss rate of water (in %) of each type of assembly ($n= 6$) registered during the curing process (28 days). Also, it is shown a photograph of the two different assemblies, made with the both evaluated mortars, where the exit of salts during the curing process can be seen.

Figure 4. Average weight loss rate of water (in %) of each type of assembly registered: a) during the first **wetting phase** ($n=2$) and b) during the second **wetting phase** ($n=2$).

Figure 5. Process of entry and advance of the moisture front during the **wetting** process with both mortars: MR (right) and MM (left). The chronological order goes from photo a to d (a: 2nd day, b: 3rd day, c: 6th day and d: 14th day). The arrows indicate the advance of the moisture front in the assembly S-MM-S, throughout the test, showing how the saline efflorescence is going in the same direction.

Figure 6. Crystallization habit observed on the surface of the assemblies with inhibitor (a) and without inhibitor (b).

Figure 7. Chloride distribution (in mg) throughout the different assemblies carried out: S-MR-S: graphs on the left and S-MM-S: graphs on the right, at different moments of the test: after curing process (a) and after the first wetting phase (b) and second wetting phase (c). The data represented in 2D, in the case of the stones, comes from the average of four samples taken at the same height (i.e. in the upper area close to the mortar, two samples taken from the stone part 1 and the other two from the stone part 2); while in the mortars the data are the average of the two samples taken at the same height.

Figure 8. SEM micrographs and EDX analyses of mortar specimens without (MR) and with ferrocyanide in its composition (MM). a) shows the cross section of the MR mortar where cubic crystals of NaCl are shown. b) shows the cross section of the MM mortar where elongated prismatic crystals of NaCl are shown.

Figure 9. SEM micrographs of sandstone samples. a) and b) show the contact surface of the sandstone with the MR mortar. c) and d) shows the contact surface of the sandstone with the MM mortar.

a) Curing process



b) Wetting process

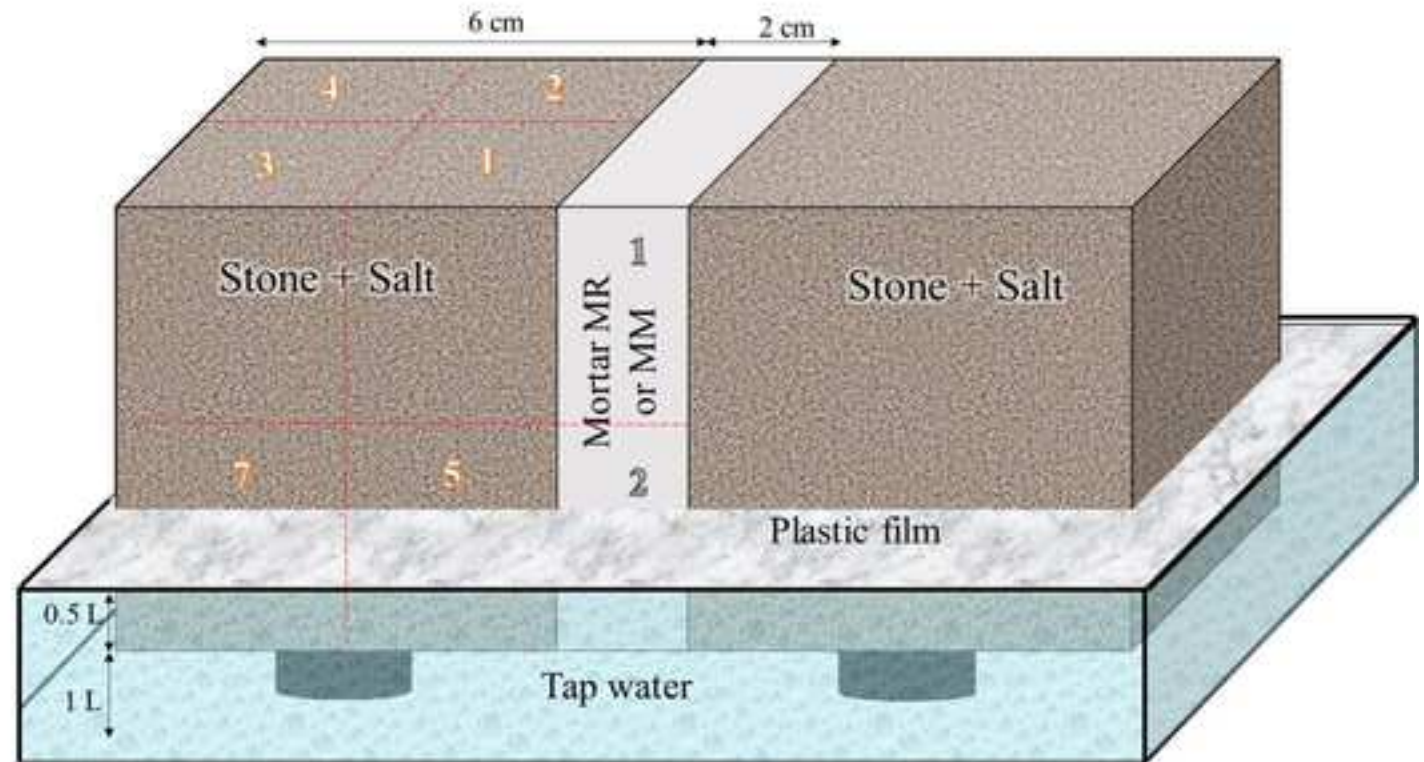


Figure 2

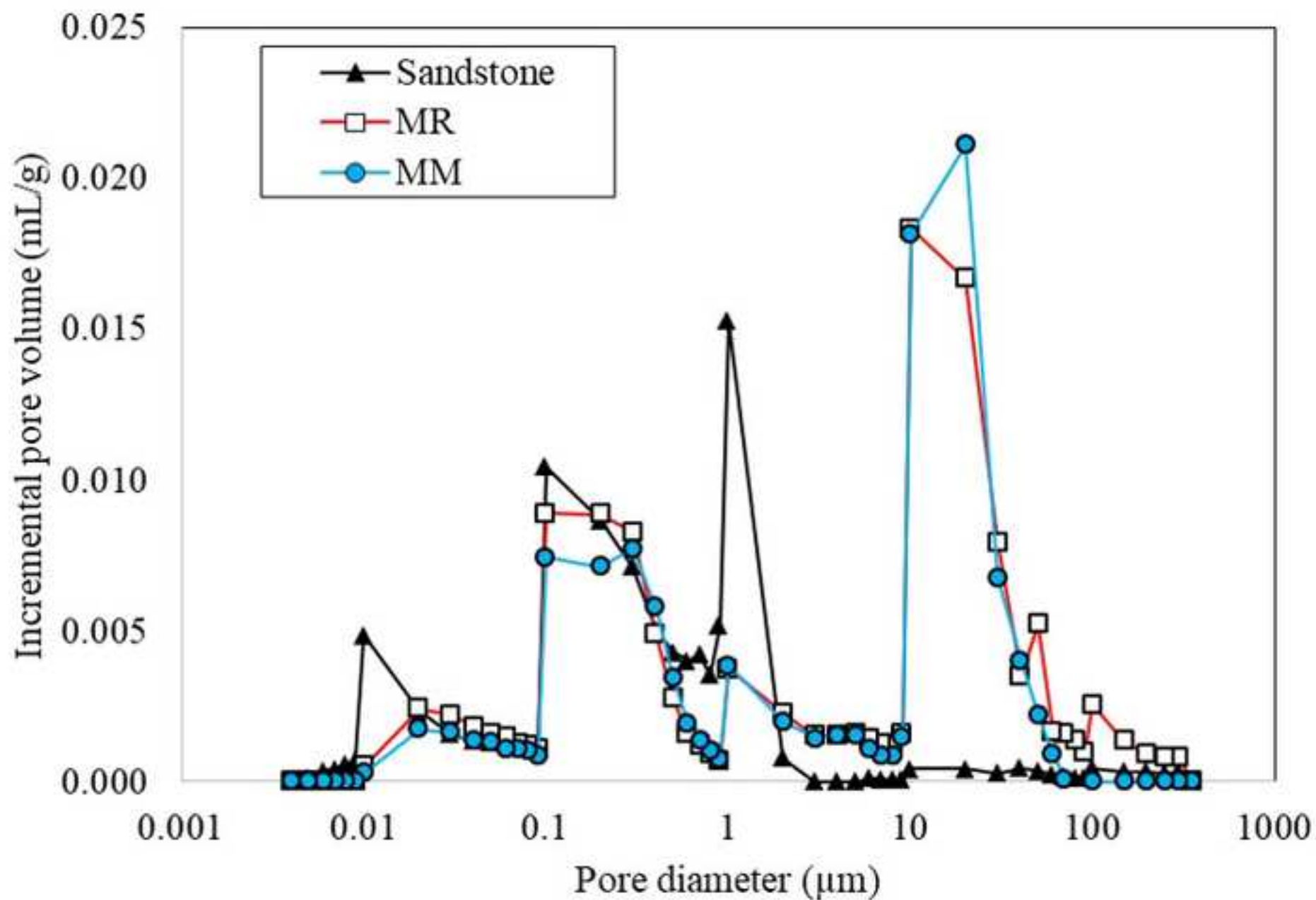


Figure 3

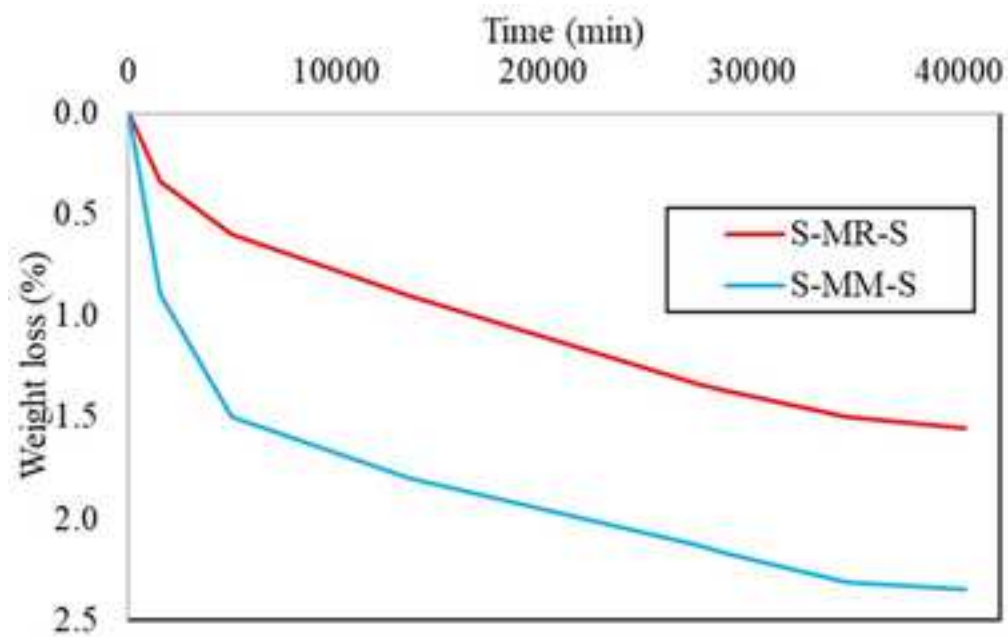
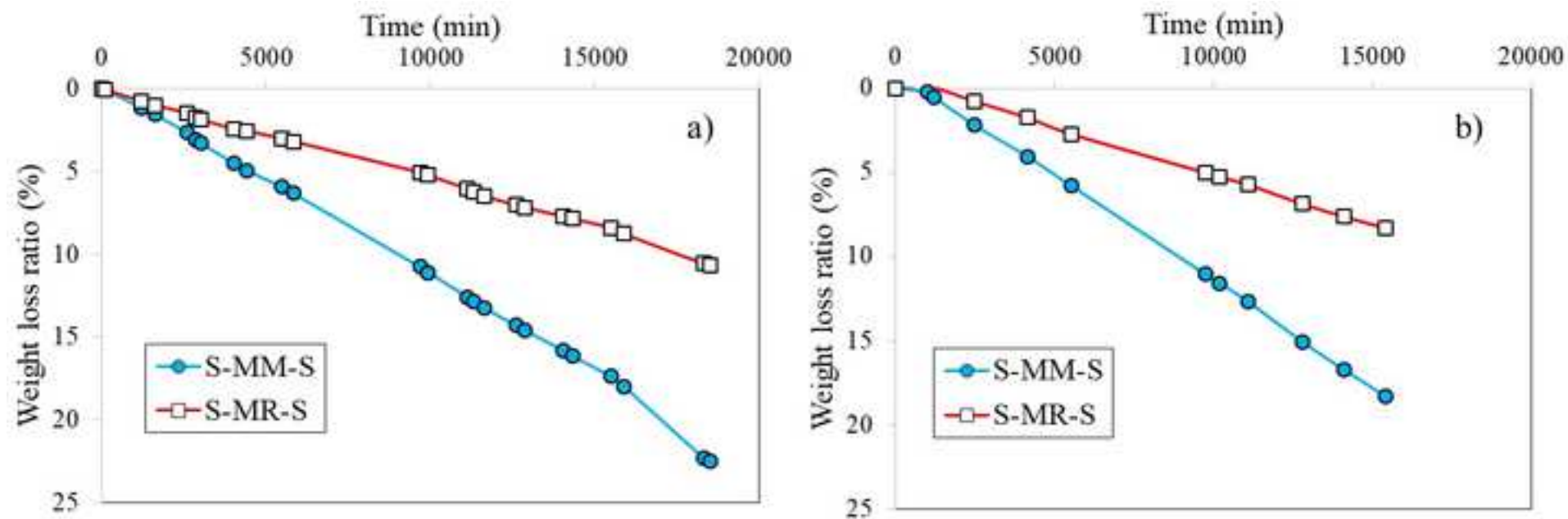


Figure 4

[Click here to access/download;colour figure;Figure 4.jpg](#)



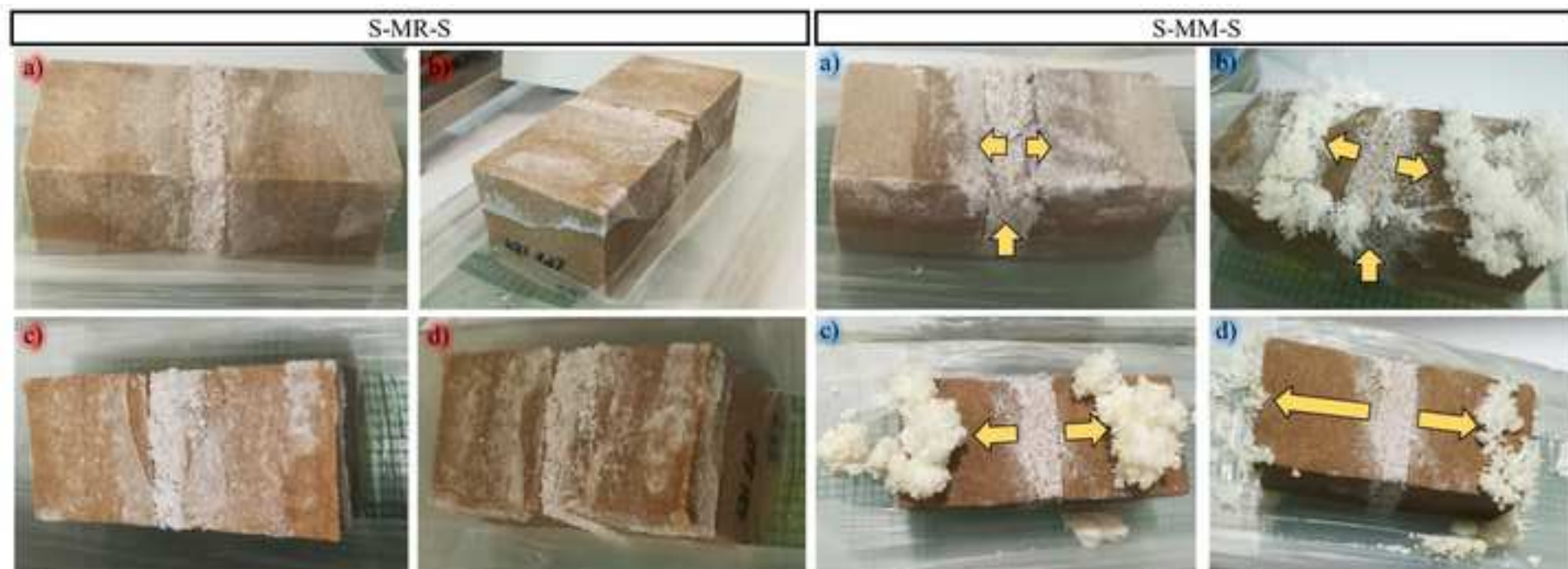
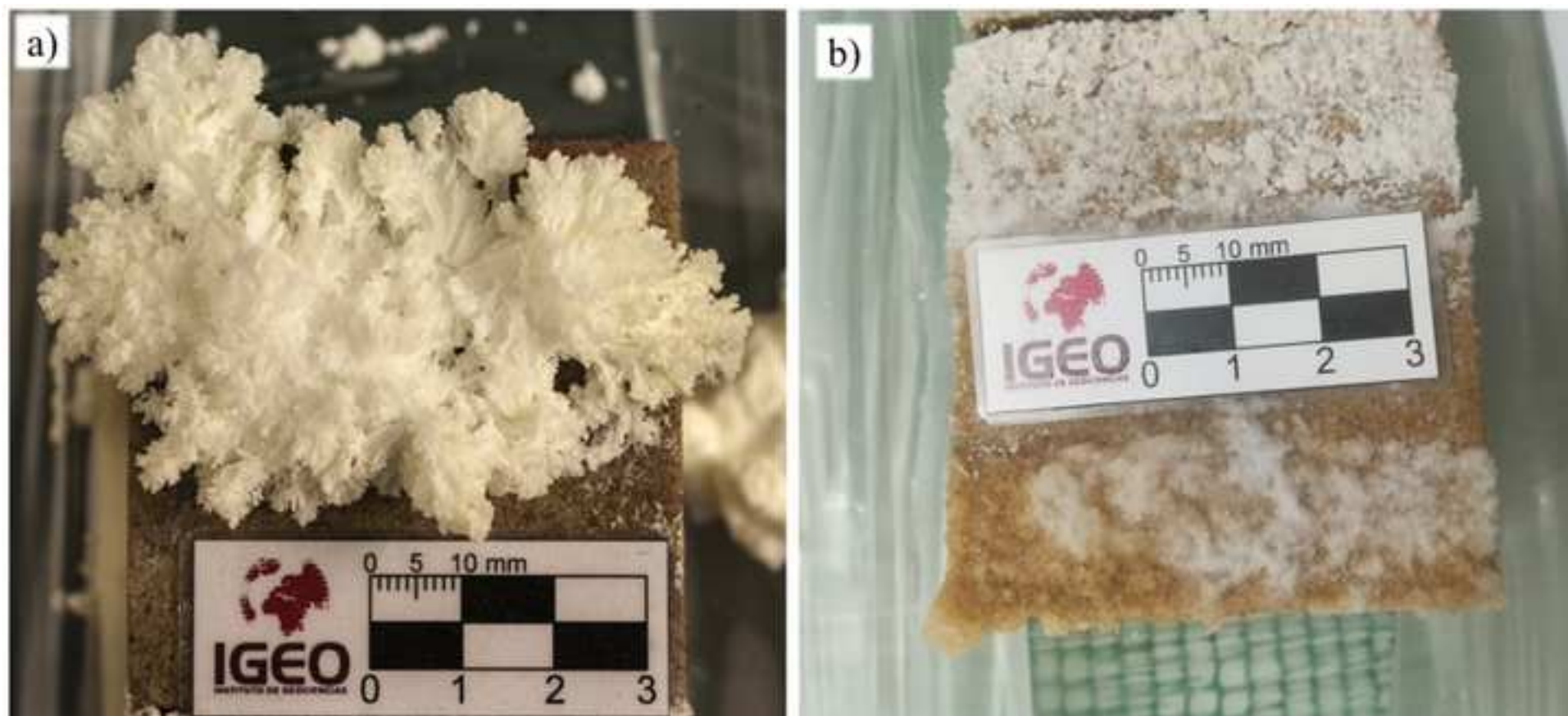
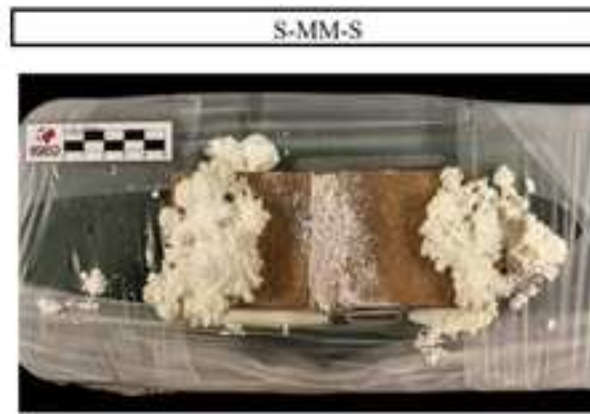
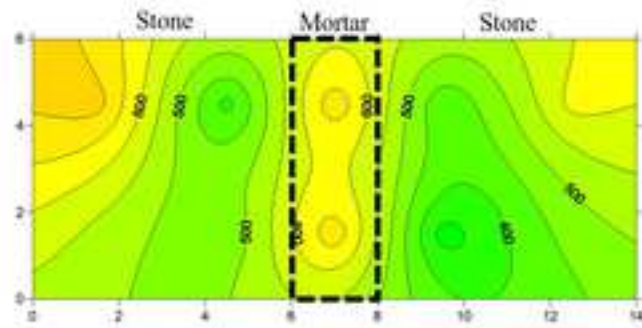
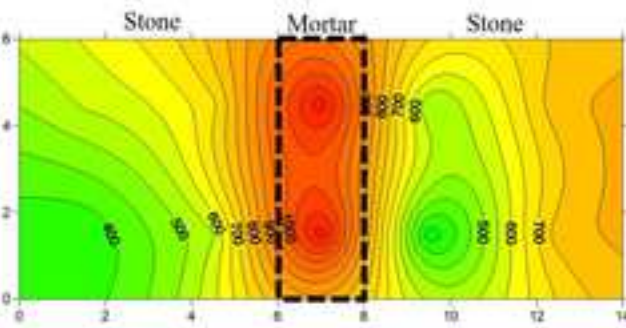
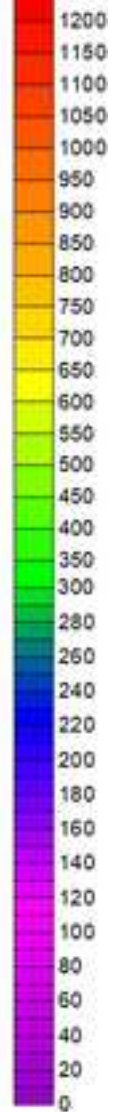


Figure 6

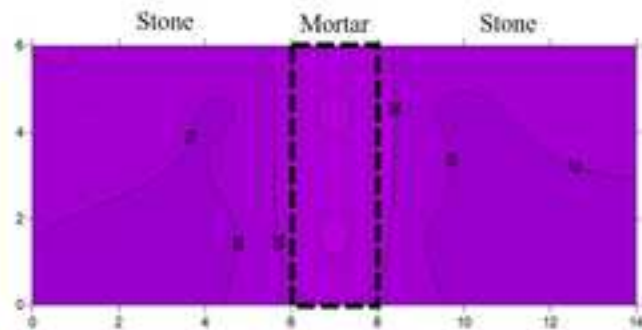
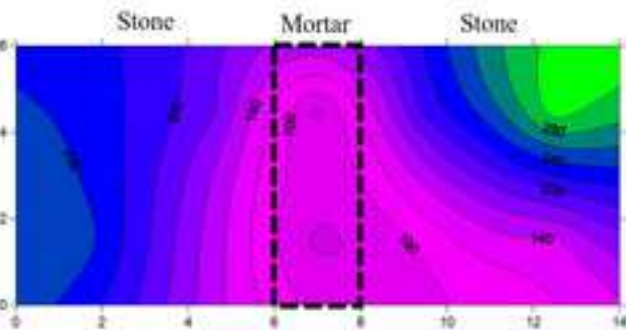




a) Curing process

mg Cl⁻

b) First Wetting Phase



c) Second Wetting Phase

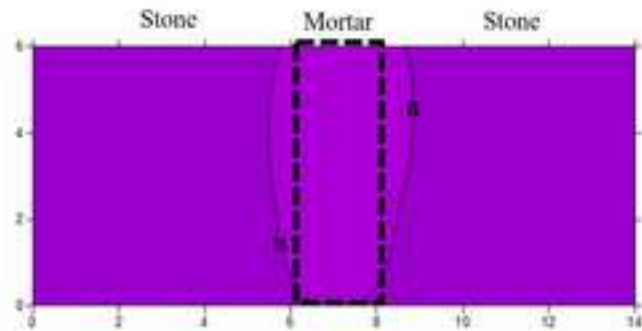
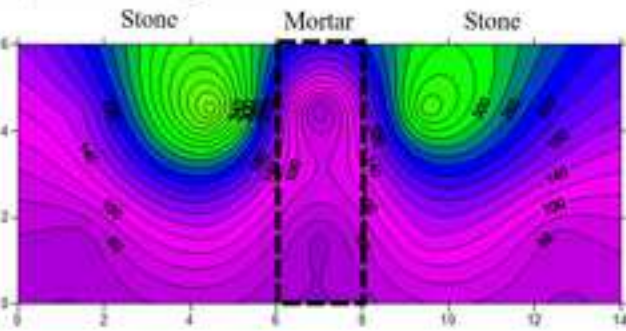


Figure 8

[Click here to access/download;colour figure;Figure 8.jpg](#)

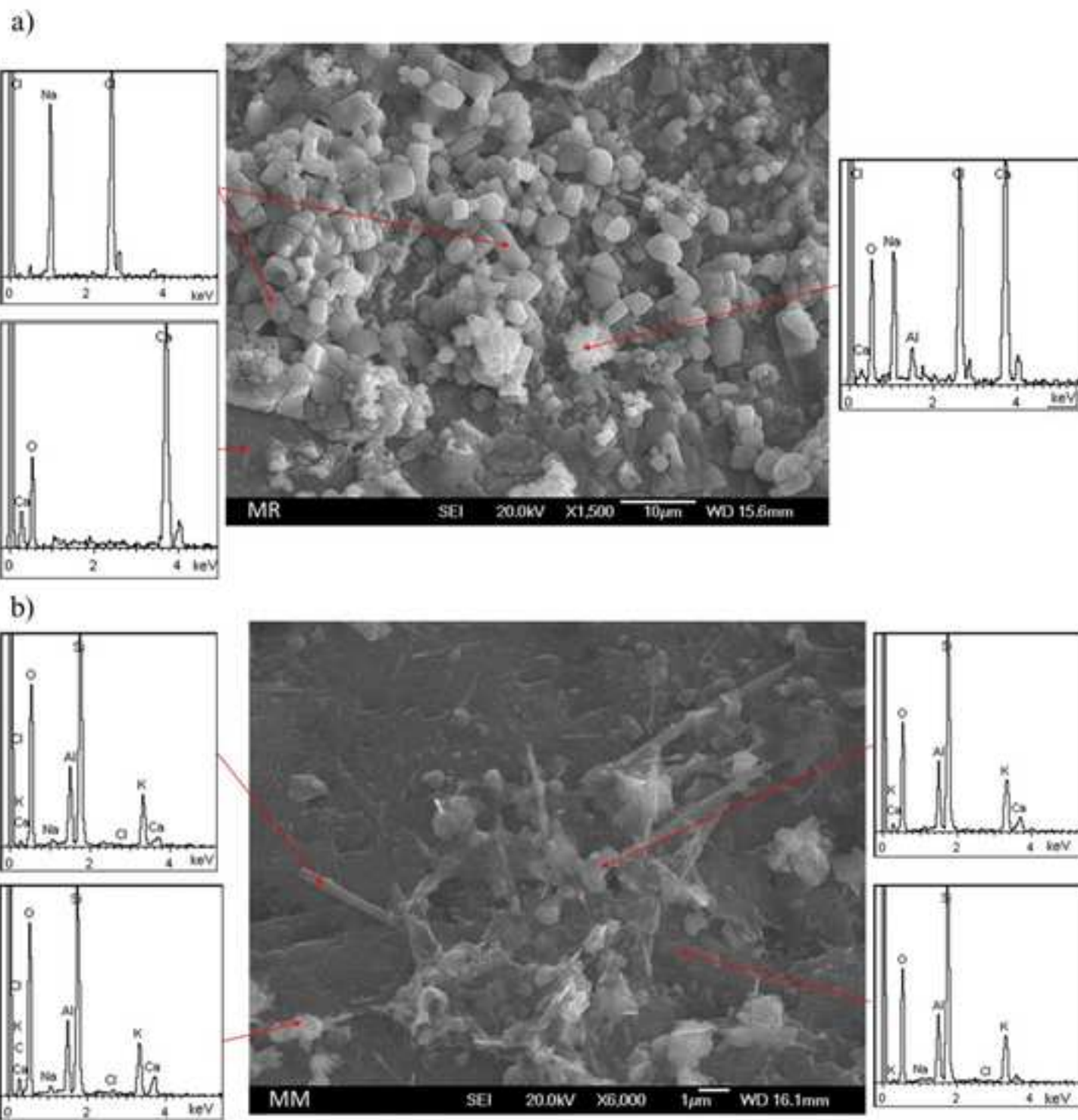


Figure 9

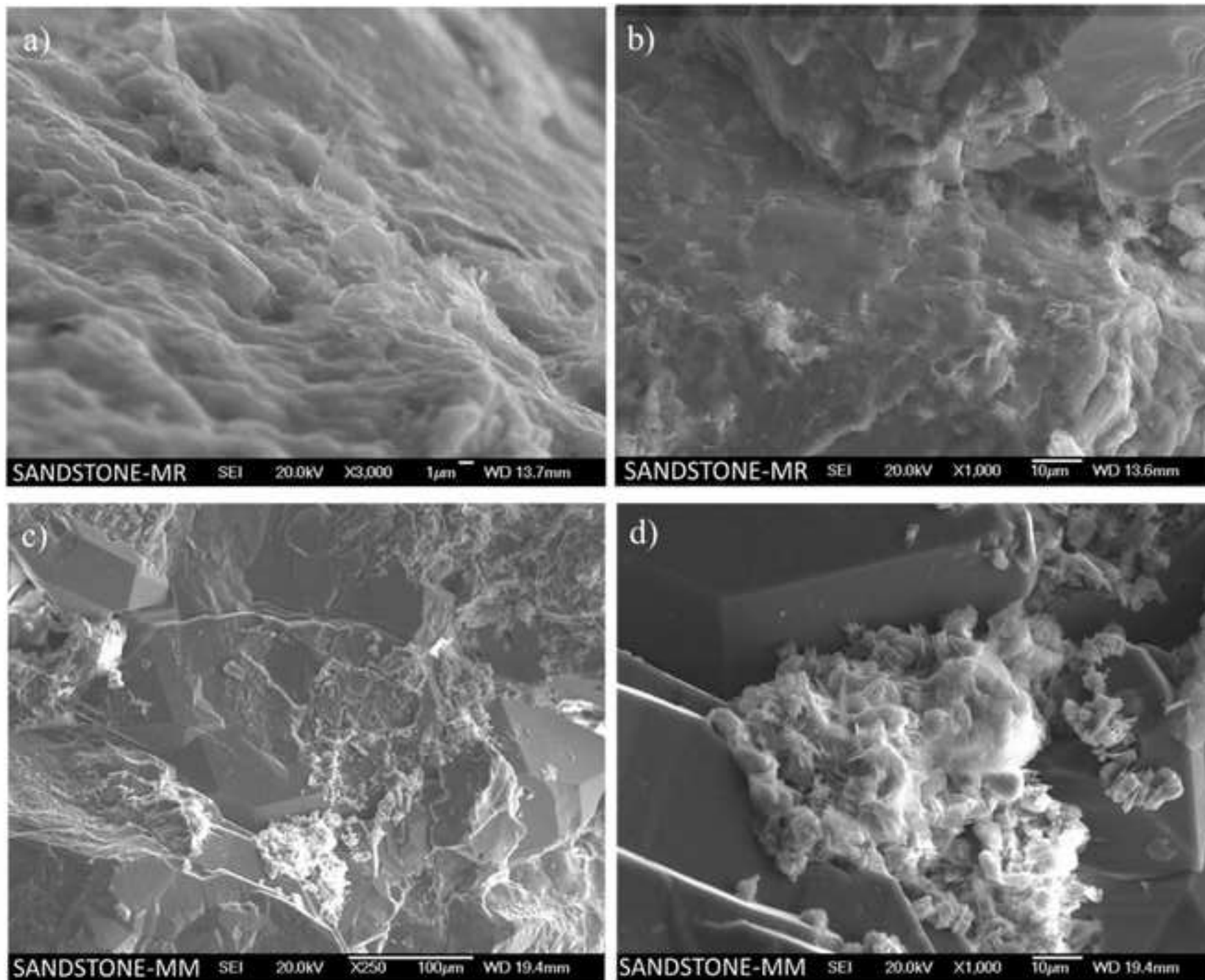


Table 1. Physical properties of sandstone and mortars, without modifier (MR) and with potassium ferrocyanide in their composition (MM).

Property	Sandstone	MR	MM
Water accessible porosity (% v/v)	14.99±0.45	28.01±0.37	28.50±0.45
Mercury accessible porosity (% v/v)	18.89	26.73	20.10
Capillary porosity (% v/v)	10.63±0.46	22.95±0.49	20.15±0.22

Table 2. Average of the total intruded mercury volume (in mL/g, n=2) and also the total intruded volumes for different pore size ranges for the sandstone and mortars without modifier (MR) and with potassium ferrocyanide in their composition (MM).

	Total	Pore size ranges (μm)				
		<0.1	0.1-1	1-10	10-100	>100
Sandstone	0.092	0.018	0.052	0.016	0.003	0.002
MR	0.131	0.014	0.038	0.016	0.057	0.006
MM	0.114	0.010	0.037	0.015	0.053	0.000

Table 3. Distribution of salts, efflorescences and subflorescences (in g and %), present in the sandstone samples joined by mortars, without (MR) and with modifier (MM) in their composition, at different moments of the test: after the curing process (1), after the first wetting phase (2) and after the second wetting phase (3).

Mortar:	MR			MM		
Test phase:	1	2	3	1	2	3
Efflorescence (g)	0.02	7.50	9.50	2.65	19.20	21.70
Subflorescence (g)	10.24	3.24	3.08	8.13	0.18	0.13
Efflorescence (%)	1.92	69.80	75.51	24.59	99.08	99.38
Subflorescence (%)	98.08	30.20	24.49	75.41	0.92	0.62

Table 4. Colorimetric differences ΔL^* , Δa^* , Δb^* , ΔC^*ab and total color difference ΔE^*ab on both materials surfaces (mortar and sandstone), due to the entry of NaCl (1: in sandstone specimens: initial color vs salinization color; in mortars: initial color vs color after curing) and after the wetting process (2: initial color vs final color).

Material	Mortar used		ΔL^*	Δa^*	Δb^*	ΔC^*ab	ΔE^*ab
Sandstone	MR and MM	1	-16.02	0.91	-2.21	-1.94	16.27
	MR	2	0.12	-0.80	-5.17	-5.23	5.24
	MM	2	1.61	-0.80	-4.35	-4.42	4.81
Mortar	MR	1	-1.37	-0.07	2.39	2.31	2.76
		2	-4.22	0.63	2.95	3.01	5.19
	MM	1	-2.17	-0.20	0.46	0.41	2.23
		2	0.72	-0.22	-0.11	-0.16	0.76