How *not to bother* salts while grouting

Chiara Pasian[1]*, Francesca Piqué[2], Cristiano Riminesi[3] and Albert Jornet[2]
[1] Department of Conservation and Built Heritage, Faculty for the Built Environment, University of Malta, Msida, Malta
[2] Institute Materials and Constructions, University of Applied Sciences and Arts of Southern Switzerland, Lugano, Switzerland
[3] Institute for the Conservation and Valorization of the Cultural Heritage (ICVBC), National Research Council, Florence, Italy
**** chiara.pasian@um.edu.mt***

Abstract

The objective of this research work was to assess if the injection of water-reduced grouts (water-ethanol-based) mobilises soluble salts to a lesser extent compared to the injection of conventional water-based grouts. Ethanol was used as a partial substitute for water in grouts preparation, being a poorer solvent for soluble salts when compared to water. Three injection grouts were evaluated; for each grout individually, the performance of mixtures prepared with 100% water was compared to the performance of the same grout prepared with water-ethanol. To assess the different performance in a salt loaded system, the grouts were tested into replicas of delaminated plaster intentionally contaminated with NaCl. The salt movement was followed by evanescent field dielectrometry using the SUSI© instrument. Grouts with reduced water content were also tested on site, at the San Vincenzo Oratory in Pazzallo, Tessin (CH), on decorated plasters afflicted by severe delamination associated with high amounts of soluble salts. Two adjoining areas, comparable in condition and in salt content, were stabilised with the same grout differing only in the nature of the suspension medium used (water-ethanol vs. water). Both in the laboratory and on site, it was experimentally verified that water-ethanol-based grouts caused a significant reduction of salts mobilisation, bothering salts to a lower extent compared to a typical water-based grouting intervention.

Keywords: injection grouting, water, alcohol, dielectrometry, SUSI©

1. Introduction and research aims

Injection grouting is an intervention aiming to stabilise and re-adhere delaminated plaster/render introducing a compatible adhesive material with bulking properties[1, 2]. Injection grouts are suspensions composed of a binder, aggregates, additives and a suspension medium, which is typically water. In lime- and hydraulic lime-based injection grouts, water is required for chemical setting as well as to improve injectability, however an excessive amount of water may lead to bleeding or segregation[3], shrinkage and thus grout failure. During grouting water is introduced in high amounts in the porous materials of the wall painting and/or historic structure (during pre-wetting and by grouting itself), potentially jeopardising water-sensitive original materials, solubilising soluble salts, and leading to their movimentation and damaging re-crystallisation. Water-reduced injection grouts were designed and studied to reduce these risks.

The objectives of this research include the evaluation of performance of designed grouts with reduced water content in relation to the solubilisation and movimentation of soluble salts in contaminated plasters. The performance of the grouts was assessed in the laboratory through evanescent field dielectrometry using SUSI© instrument* (C. Riminesi and R. Olmi, Diagnostics and monitoring

* *Acronym for Sensore per la misura di Umidità e Salinità Integrato, integrated sensor for measuring humidity and salinity.*

of moisture and salt in porous materials by evanescent field dielectrometry, 4th International Conference on Salt Weathering of Buildings and Stone Sculptures, Potsdam 20-22.9.2017), and on site, at the San Vincenzo Oratory in Pazzallo, Tessin (CH), on decorated plasters afflicted by severe problems of delamination associated with high amounts of soluble salts.

2. Materials and mixtures

Three injection grouts were evaluated: two hydraulic lime-based pre-mixed commercial grouts (PLM A CTS and LEDAN RI.STAT BASE B TecnoEdile Toscana) and one slaked lime-based grout designed in our laboratory (called in this paper grout C).[4] Grout C was formulated with the following components and proportions in parts by volume (pt/V): 1 pt/V slaked lime putty, 1.5 pt/V quartz sand (Ø < 740 µm), 1 pt/V pozzolan (pozzolana flegrea), 0.6 pt/V ammonium carbonate, and 0.1 pt/V plasticiser (Sika Viscocrete-2S, Sika AG) [4]. Ammonium carbonate, which naturally decomposes releasing carbon dioxide, was added to provide carbon dioxide to help carbonation in the deficiency of air (void in depth). The slaked lime used in this research is composed of ca. 50% $Ca(OH)_2$ – 50% water (in weight), determined gravimetrically.

The grouting mixtures were prepared using as suspension medium water (control) or water-ethanol mixed in different proportions. Alcohols are less effective solvents for ionic substances such as soluble salts when compared to water, as they have the polar hydroxyl group (–OH) and a non-polar chain. Ethanol was selected as a partial substitute for water because of its miscibility with water and because it is a poor solvent for salts.[5, 6]

The amount of suspension medium to prepare the grouts (mL suspension medium/g dry pre-mixed grout or g slaked lime) used for this research is significantly lower compared to the water amount suggested in the technical data sheets of PLM A and LEDAN RI.STAT BASE B. In the suspension medium to prepare the grouts, the amount of water was progressively decreased. The three suspension media selected were: 100% water ('control' representing the traditional grouts preparation), 50% water: 50% ethanol, 25% water: 75% ethanol.[4] PLM A and LEDAN RI.STAT BASE B required the addition of a filler (quartz sand, inert and non-porous) when mixed with water-ethanol to obtain a cohesive grout with no shrinkage.[4]

Set grout performance and working properties of the water-reduced grouts were tested in the laboratory following international standards and tests specifically designed for injection grouts.[7] The grouts mixed with water-ethanol showed adequate shrinkage, porosity, cohesion, and adhesion in replicas of delaminated plaster, as well as good injectability, and therefore they are potentially suitable for implementation on site.[4]

3. Soluble salts movement – Assessment in the laboratory

In order to assess the mobilisation and solubilisation of salts while grouting, replicas of delaminated plaster intentionally contaminated with NaCl were prepared. The effects of the injection into such replicas of water-ethanol grouts were compared with those of water-based grouts.

3.1. Materials and methods

As ethanol is a poorer solvent for soluble salts when compared to water[5, 6], the injection of water-ethanol-based grouts should solubilise salts in the delaminated plaster to a lesser extent compared to the injection of water-based grouts. This was verified in the laboratory with SUSI©* system (acronym for Sensore per la misura di Umidità e Salinità Integrato, integrated sensor for measuring humidity and salinity). SUSI© is an instrument based on Evanescent Field Dielectrometry (EFD), which is a technique deriving from dielectric spectroscopy.[8] SUSI© works in the microwave range (1-1.5 GHz), it is portable and allows real-time non-invasive measurements of sub-surface moisture content (MC) and the detection of soluble salts (SI, i.e. salinity index). The values of MC and SI can be separately and independently measured by the instrument. The moisture content (MC) of porous materials such as plaster is measured due to the dielectric contrast between water and the host material (plaster).[9] The water content which can be measured ranges between 0 and 20% (water volume fraction); the range of salinity index varies between 1 and 10 from no-salt to saturated salt conditions.[10] SI is a measure of the salt ions present in solution in the host material.

Replicas of delaminated plaster were prepared (in stratigraphy: brick, coarse plaster composed of slaked lime : sand 1:3 pt/V, fine plaster composed of slaked lime : sand 1:2 pt/V). The delamination (void) was produced between the coarse and the fine plaster, using the following procedure: the coarse plaster was applied on a brick tile; on this plaster, in the middle of the tile, small cylinders of dry-ice (solid CO_2) were stacked together in the shape of a truncated pyramid; the second plaster layer (fine plaster) was applied on the dry-ice cylinders. As the dry-ice sublimes, an empty void between the two plaster layers is created.[4] The fine plaster was contaminated with 0.5% NaCl (0.5% of the weight of the sand used to prepare the plaster and 0.7% of the total weight of the plaster).

The grouts chosen for the experiment were the grouts with the least amount of water (25% water : 75% ethanol) vs. the controls (100% water).

* *Pat. CNR n. 1626 – FI 2004A000187.*

3.2. Calibration – Determination and correction of ethanol contribution

SUSI© typically works in presence of water to determine MC and SI. In this research the authors wanted to assess the solubilisation of salts in presence of a water-ethanol grout, therefore a new calibration of the instrument was needed.

Samples (10 cm x 10 cm and 2 cm thick) made of the same plaster of the replicas (fine plaster, slaked lime : sand 1:2 pt/V) were prepared. 9 plaster samples were prepared with no soluble salts and 9 analogous samples were prepared with plaster contaminated with 0.5% NaCl (0.5% of the weight of the sand used to prepare the plaster and 0.7% of the total weight of the plaster). The samples were immersed in three different solutions: 100% water, 50% water : 50% ethanol and 25% water : 75% ethanol. In each solution 3 non-contaminated samples and 3 contaminated samples were immersed. The samples were kept lifted from the bottom of the container with the solution through glass rods; the samples were immersed in the solution up to the height of 1 cm of their total thickness.

For every sample, MC and SI were measure at t0 (dry samples); after the samples were placed in the solutions, for each sample MC and SI were monitored at 30 seconds interval until complete saturation. The time for complete imbibition was recorded for each sample. A calibration of the instrument taking into consideration the contribution of ethanol, with and without soluble salts, was performed.

3.3. Injection of water-reduced grouts into contaminated replicas

Six replicas of delaminated plaster *(see Section 3.1)* were prepared.[4] The following grouts were injected, one for each replica:

1) PLM100-0 (100% water) vs. PLM25-75 (25% water : 75% ethanol)
2) LEDAN100-0 (100% water) vs. LEDAN25-75 (25% water : 75% ethanol)
3) C100-0 (100% water) vs. C25-75 (25% water : 75% ethanol)

Before the injection, measurements with SUSI© of MC and SI were performed on the dry replicas. The replicas were placed in a vertical position to simulate the injection into a wall. Before injecting the grout, replicas were pre-wetted. Pre-wetting is performed to clear the cavity and to wet the internal surfaces of the void, with the aim of reducing the absorption of the liquid contained in the grout mix and reduce grout shrinkage.[4] The pre-wetting liquid employed for each replica was the one used to prepare each grout respectively (100% water for grouts PLM100-0, LEDAN100-0 and C100-0; 25% water : 75% ethanol solution for grouts PLM25-75, LEDAN25-75 and C25-75). Measurements of MC and SI were performed with SUSI© immediately after pre-wetting. Injection of the grout was then performed, one grout in each replica *(Fig. 1)*.

After the injection, measurements of MC and SI were performed *(Fig. 2)*: immediately after the injection; at 10 minutes interval within the first hour, after 2, 3 and 4 hours, after 24, 48 and 72 hours. In this way, variations of MC and SI could be followed over time for each replica.

Figure 1: Injection of grout PLM25-75 into the replica of delaminated plaster

Figure 2: SUSI© measurements on a replica after 48 hours from the injection

3.4. Discussion

Graphs in *Fig. 3a-f* show the variation of MC and SI over time for each replica. For each grout typology (respectively PLM, LEDAN and grout C) it is visible that MC is much higher for grouts prepared with 100% water (controls) compared to grouts prepared with water-ethanol *(Fig. 3a-c-e)*. This was predictable, as MC indicates the water volume fraction in the host material (plaster).

More interesting are the results concerning SI *(Fig. 3b-d-f)*; for all grouts the mixture prepared with 25% water : 75% ethanol (red in the graphs) has a much lower SI compared to the control prepared just with water (black in the graphs). This because a 25% water : 75% ethanol solution solubilises salts to a lesser extent compared to water.[5, 6] Data regarding SI are presented in *Table 1*:

Grout	Range of SI over time
PLM100-0	2.0 – 8.5
PLM25-75	2.2 – 4.0
LEDAN100-0	2.3 – 6.5
LEDAN25-75	1.0 – 3.8
C100-0	2.3 – 5.5
C25-75	0.0 – 1.8

Table 1: Range of salinity index (SI) over time of the replicas

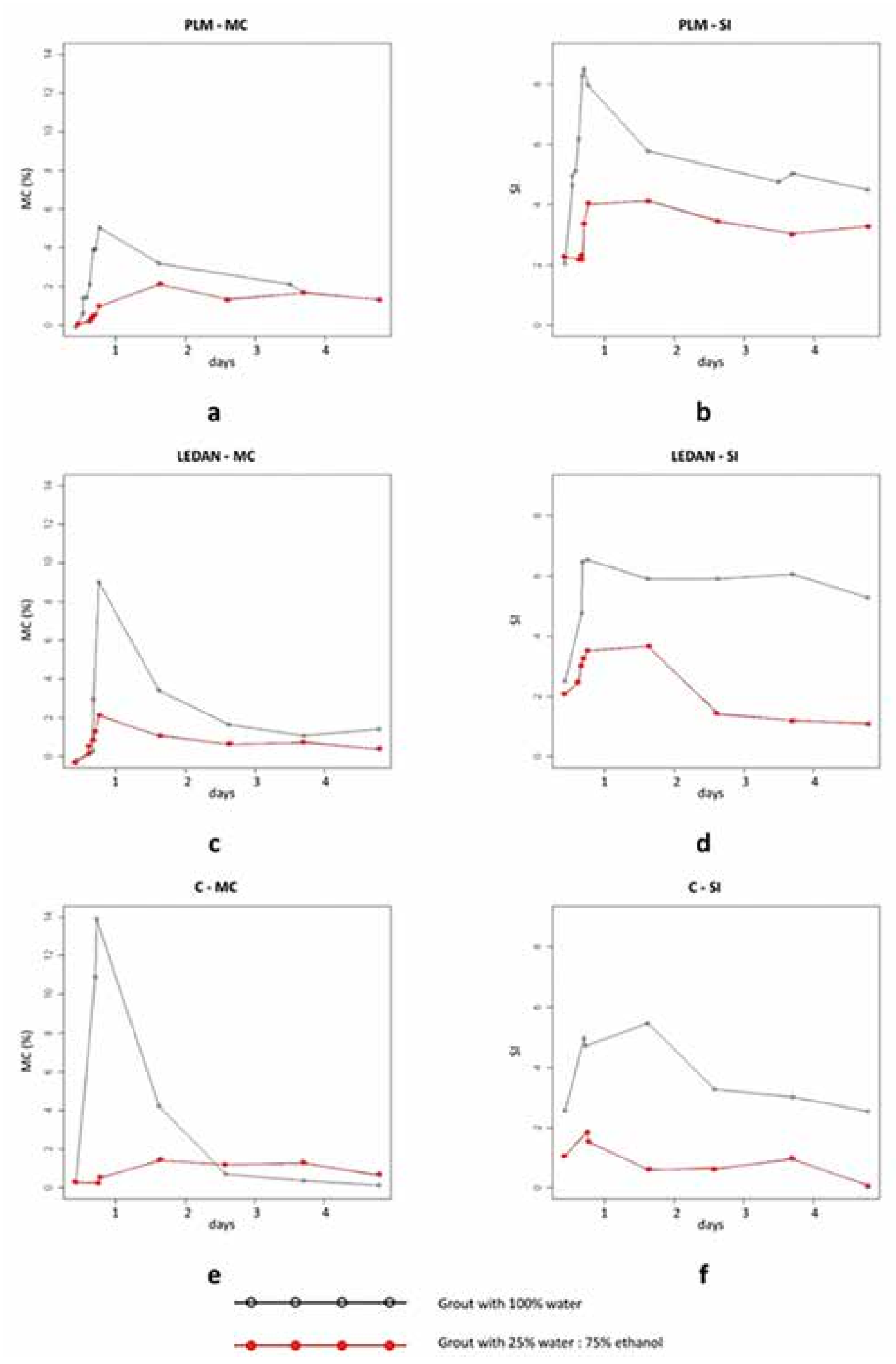

Figure 3: Graphs showing MC (3a PLM, 3c LEDAN, 3e grout C) and SI (3b PLM, 3d LEDAN, 3f grout C) over time, from to (dry replica) to 72 hours after the injection. The first point of measure on the graph is performed on the dry replica, the second point immediately after pre-wetting, the third point immediately after the grout injection; measures are then taken at 10 minutes interval within the first hour, after 2, 3 and 4 hours, after 24, 48 and 72 hours

The maximum value of SI after the injection of PLM25-75 is less than half compared to the maximum value after the injection of the control (PLM100-0). The maximum value of SI after the injection of LEDAN25-75 is about 2/5 lower compared to the maximum value after the injection of the control (LEDAN100-0). Values referred to grout C25-75 are particularly low (maximum value of SI 1.8): the maximum value measured for C25-75 is about 1/3 of the maximum value measured for the control (C100-0).

To increase wetting and reduce the overall provision of water, pre-wetting is often performed by conservators with a solution of water and alcohol[4], typically followed by the injection of a water-based grout.

The graphs reporting the measures performed with SUSI© show that the injection of grouts prepared with 25% water : 75% ethanol (after pre-wetting with the same solvent mixture) solubilises salts in the replicas to a lower extent compared to the injection of the same grouts prepared with 100% water.

4. On site application of grouts with reduced water content

Grouts with reduced water content were tested on site, at the San Vincenzo Oratory in Pazzallo, Tessin (CH). The Oratory, decorated with wall paintings and stuccoes and dated to the XVIII c., was abandoned in the last decades and it is affected by severe problems of delamination associated with high amounts of soluble salts. The north wall of the Oratory was the most affected by problems deriving from soluble salts and high humidity (RH constantly around 80% with 19-21°C T in the months during which the research was carried out; environmental monitoring by A. Kueng, SUPSI). The north wall is adjacent to a building which used to be a cowshed and which was thus a vehicle for nitrates.

The pilaster located on the north wall of the Oratory presented delamination between the brick support and the coarse plaster *(Fig. 4)* affecting an area of approximately 30x80 cm and 3 cm thick. Diffuse salt efflorescence was present both inside the delamination void and on the plaster surface; the salts present were identified as manly composed of nitrokalite (KNO_3 – equilibrium relative humidity 94.6% at 20°C [11]) (A. Kueng, SUPSI, internal report).

This area was considered suitable for testing and comparing the effects of reduced water grouts with those of regular grouts.

Figure 4: Delaminated pilaster in San Vincenzo Oratory, north wall

4.1. Objectives, materials and preliminary testing

The objective of the application on site was to verify that also in a real case the injection of a grout prepared with water-ethanol mobilises salts to a lesser extent compared to the injection of a grout prepared just with water.

A piece of plaster, already detached inside the delamination, was extracted; its porosity was measured in the laboratory (standard SIA 262/1:2003 [12]) as well as its compressive strength (standard UNI EN 1015/11 [13]). The porosity and the compressive strength of the original plaster were compared with those of the grouts with reduced water content, tested in the laboratory with the same standard procedures. The injection grout with the compressive strength most similar to that of the original plaster was PLM prepared with 25% water : 75% ethanol (PLM25-75) *(see Table 2)*. PLM25-75 has a higher porosity compared to that the original plaster *(see Table 2)*; this is considered good because the porosity of the injection grout should be similar or higher to that of the original material [1].

	n (%) tot. por.	UE (%) capill. por.	LP (%) air pores	σc (N/mm2) compr. strength
Original plaster	35.2	28.5	6.7	3.24
PLM25-75	46.4	39.7	6.7	3.57

Table 2: Porosity and compressive strength of the original plaster and grout PLM25-75

4.2. Intervention

The lowest part of the delaminated pilaster, an area of 30 cm width x 20 cm height (delamination 3 cm thick) was chosen for the test. This area was about 40 cm above the ground. The salts distribution in a wall is extremely heterogeneous both on the surface and in depth. In particular, in the case of capillary rising damp, ions are distributed in the wall in different concentrations also according to the height from the ground[11]; therefore it is preferable to compare two areas at the same height from the ground.

Before performing the intervention, crystallised salts were removed from the surface (area of 600 cm2) with a dry brush and weighed (0.26 g). Salt efflorescence was evenly distributed on the surface. Salts were also removed with a dry brush inside the delamination aided by a mini vacuum cleaner, which allowed removing both salts and dust inside the void.

The selected area was divided vertically by placing in the middle of the delamination a piece of foam rubber (3 cm x 20 cm, 3 cm thick as the delamination itself) to create a barrier. In this way the two grouts (PLM100-0 and PLM25-75) could be injected in the two separate chambers created in the delamination area at the same height *(Fig. 5)*.

The intervention was followed with a thermocamera (Agema 570 Thermovision PRO). The two different areas were monitored before the intervention, during the pre-wetting (performed for both areas with a solution 25% water : 75% ethanol), during the injection respectively of PLM100-0 and PLM25-75, and af-

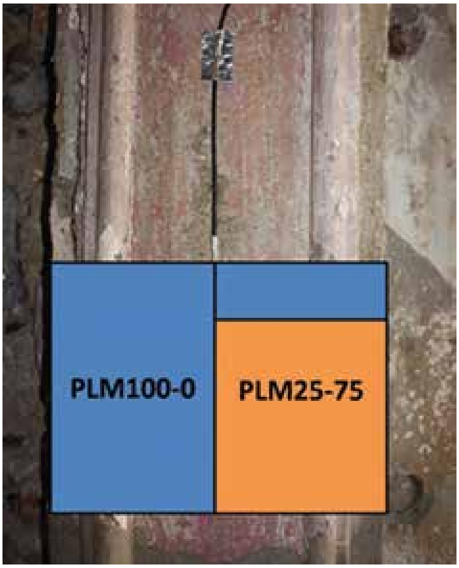

Figure 6a: Thermoimage after the injection of PLM100-0

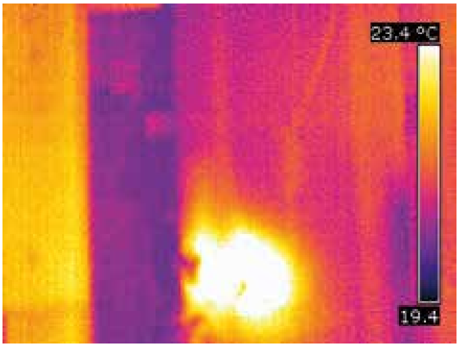

Figure 6a: Thermoimage after the injection of PLM100-0

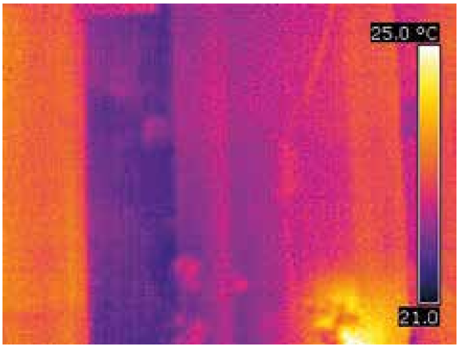

Figure 6b: Thermoimage after the injection of PLM25-75)

ter the injection over time to follow the grouts setting (every 5 minutes for the first hour; 2, 3, 4 hours after the injection; 24 and 48 hours after the injection). In order to better assess the positioning of the grouts in the delamination *(Fig. 6)*, the grouts were both slightly heated in a water bath prior to injection. In Fig. 6a PLM100-0 is more clearly visible compared to PLM25-75 *(Fig. 6b)* because it was possible to heat it longer (PLM25-75 is ethanol-based: it could not be heated long because its suspension medium is more volatile than water). It was verified that the positioning of two grouts injected in the delamination was kept separate by the foam rubber, as planned.

4.3. Assessment

After two months, the salt crystallisation was assessed on the surface of the pilaster where the intervention was performed. Salt efflorescence was removed with a dry brush in the two separate but equivalent areas (where grout PLM100-0 and where grout PLM25-75 were injected) and separately weighed. In the area where the water-ethanol-based grout PLM25-75 was injected the salt crystallisation was about 40% less (in weight, 0.12 g) compared to the area where the water-based grout PLM100-0 was injected (0.21 g).

5. Final discussion and conclusions

Injection grouts with reduced water content were evaluated, comparing the water-ethanol-based grout (25% water : 75% ethanol) with the correspondent control (100% water). In the present research their performance in terms of salts mobilisation was assessed:

- in the laboratory with SUSI© on replicas of delaminated plaster contaminated with NaCl

- on site in a limited area of intervention affected by delamination and severe soluble salts problems

In the laboratory, all the replicas injected with the water-ethanol-based grout showed a much lower salinity index (SI) compared to replicas injected with the correspondent water-based grout (control). This verified because a lower amount of salts was brought in solution by the water-ethanol grout suspension medium compared to the 100% water grout suspension medium. The data of SI measured with SUSI© prove that water-ethanol-based grouts solubilise salts to a much lesser extent compared to water-based grouts.

In the limited area treated on site, the injection of a water-ethanol-based grout led to a much lower salts re-crystallisation on the plaster surface compared to the injection of the water-based control.

Water-reduced grouts (25% water : 75% ethanol) proved to be suitable for site implementation with the advantage of bothering salts to a lower extent compared to a typical water-based stabilisation intervention.

Acknowledgements

We would like to thank Dr Christian Paglia, director of the Institute Materials and Constructions (SUPSI), allowing the conduction of the tests at the IMC. Many thanks to Andreas Kueng (IMC, SUPSI), who performed the salts analyses and the environmental monitoring in San Vincenzo Oratory. Thanks are also due to Prof Tiziano Teruzzi (IMC, SUPSI) for his help in the use of the thermocamera.

References

[1] I. Griffin, Pozzolanas as Additives for Grouts: An Investigation of Their Working Properties and Performance Characteristics, Studies in Conservation 49 (1) (2004) 23-34.

[2] S. Rickerby, L. Shekede, Fan Zaixuan, Tang Wei, Qiao Hai, Yang Jinjian, F. Piqué, Development and Testing of the Grouting and Soluble-Salts Reduction Treatments of Cave 85 Wall Paintings, in: Conservation of Ancient Sites on the Silk Road. Proceedings of the Second International Conference on the Conservation of Grotto Sites, Mogao Grottoes, Dunhuang, People's Republic of China, June 28-July 3, 2004, Ed. N. Agnew. Getty Conservation Institute, Los Angeles, 2010, pp. 471-479.

[3] B. Biçer Şimşir, I. Griffin, B. Palazzo-Bertholon, L. Rainer, Lime-based injection grouts for the conservation of architectural surfaces, Reviews in Conservation 10 (2009) 3-17.

[4] C. Pasian, F. Piqué, A. Jornet, Non-structural injection grouts with reduced water content: Changes induced by the partial substitution of water with alcohol, Studies in Conservation 62:1 (2017) 43-54.

[5] S.P. Pinho, E.A. Macedo, Solubility of NaCl, NaBr, and KCl in water, methanol, ethanol, and their mixed solvents, Journal of Chemical & Engineering Data 50 (2050) 29-32.

[6] A. Kolker, J. de Pablo, Thermodynamic Modelling of the Solubility of Salts in Mixed Aqueous-Organic Solvents, Industrial & Engineering Chemistry Research 35 (1996) 228-233.

[7] B. Biçer-Șimșir & L. Rainer, Evaluation of Lime-Based Hydraulic Injection Grouts for the Conservation of Architectural Surfaces – A Manual of Laboratory and Field Test Methods, Los Angeles: The Getty Conservation Institute, 2013.

[8] R. Olmi, M. Bini, A. Ignesti, S. Priori, C. Riminesi, & A. Felici, Diagnostics and monitoring of frescoes using evanescent-field dielectrometry, Measurement Science and Technology, 17:8 (2006) 2281.

[9] R. Olmi & C. Riminesi, Study of water mass transfer dynamics in frescoes by dielectric spectroscopy, Il Nuovo cimento della Società Italiana di Fisica C 31:3 (2008) 389.

[10] N.Proietti, D. Capitani, V. Di Tullio, R. Olmi, S. Priori, C. Riminesi, A. Sansonetti, F. Tasso & E. Rosina, MOdihMA at Sforza Castle in Milano: Innovative Techniques for Moisture Detection in Historical Masonry. In Built Heritage: Monitoring Conservation Management 2015, pp. 187-197, Springer International Publishing.

[11] K. Zehnder & A. Arnold, Monitoring wall paintings affected by soluble salts, in: The Conservation of Wall Paintings, ed. S. Cather, The Getty Conservation Institute, Marina del Rey, 1991, 103-108.

[12] SIA 262/1 2003, Perméabilité à l'eau, Construction en Béton–Spécifications complémentaires, Société suisse des ingénieurs et des architectes, Zurich.

[13] UNI EN 1015/11 1999, Methods of Test for Mortar for Masonry–Part 11, Determination of Flexural and Compressive Strength of Hardened Mortar, Milano.