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Monitoring the removal of soluble salts from ancient tiles by ion chromatography

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Abstract

The application of ion chromatography, conductometry and total carbon analysis to the study of desalination of 18th century tiles and mortars is described. Ion chromatography is shown to be a simple and adequate technique for the identification and quantitative analysis of ions which are extracted during desalination. Chloride, nitrate, sulphate, carbonate, sodium, potassium, calcium and magnesium were always found in the immersion waters, and occasionally also nitrite and oxalate.

Keywords: Ceramics; Tiles; Inorganic cations; Inorganic anions

1. Introduction

Tiles have occupied an important place in Portuguese culture and their use has been constant throughout the last five centuries. Thousands upon thousands of tiles were produced and applied as panels in both the interiors and the exteriors of private and public buildings as well as in the covering of whole facades. Due to a number of factors, this vast inheritance has been suffering serious degradation.

Little attention has been focused on how tiles deteriorate. In fact, tiles are relatively durable glazed ceramics but they are susceptible to damage by brittle fracture, abrasion and salt precipitation. The damage of ancient tiles by soluble salts is the most difficult to assess: salts accumulate underneath the glazed surface, and recrystallize, with an increase in

volume. The mechanical forces so produced, in combination with chemical effects that are still poorly understood, can ultimately detach the glaze from the underlying ceramic body.

Underground water can be absorbed through the walls where tile panels are applied. Rain water may also be introduced through the roofs of ancient buildings and the presence of salts of biological origin—particularly NaCl and KNO₃, and eventually also of sulphate—cannot be ignored. Accordingly, one of the important steps in restoration/consolidation procedures for ancient tiles is the removal of soluble salts by immersion in deionized water. Traditionally this process has been monitored by conductometric measurements. However, the identification of removed ions is important to understand the degradation mechanisms, select restoration and preservation procedures and take some sort of action to avoid future damage. By using ion chromatography to identify and quantify the ions present one can also

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monitor the evolution of salt concentration during the desalination procedure.

Although a number of studies and articles have been written on salt damage to stone [1–4], ceramic materials (e.g. [5,6]) and desalination [7–9], reliable methods for evaluating the degree of damage and the most effective treatment to remove them without further deterioration have not been developed for tiles.

The present study involves the determination of anions and cations removed from 18th century tiles and mortars from Igreja de S. Salvador (Coimbra, Portugal) by immersion of the tiles (and mortars) in deionized water. In this Portuguese church tiles almost completely cover the walls and restoration works started in 1995. Most tiles were in a poor state of preservation showing a countless number of fractures, fissures, crazing and detachment of the glaze. Around 25% were missing, or extremely deteriorated, mainly due to salts of several origins. There were many signs of repairs and crude rebuildings and several different types of mortars have been used in these previous restoration works.

Conductometry is a convenient technique to study the removal of salts as it can easily be applied to monitor the total ionic concentration in the water of immersion. It has been previously applied to studies with ceramics [8] and tiles [5,10,11]. Atomic absorption spectrometry has been occasionally used for Ca^{2+} analysis in desalination of ceramic materials [5]. For stone and mortars classical analytical methods such as determination of Cl^- with silver nitrate [12,13], analysis of sulphate as BaSO_4 by addition of BaCl_2 [13], and the use of specific electrodes (for Cl^-) [14] have been reported. Methods of analysing the solid salts occurring on stones, mortars and mural paintings combining optical mineralogy with classical microchemical slide tests have also been described [15].

We report results on the use of suppressed ion chromatography and as a simple means for the qualitative and quantitative determination of ions as they are removed from tiles during desalination procedures. Some of the analysis of anions of soluble salts removed from 17th century tiles from the S. Bento panel (S. Bento palace, Lisbon, Portugal) have been recently reported [16–18]. These suggest that conductivity may receive a significant contribution

from carbonate due to erosion of the ceramic body of the tiles. The monitoring of the carbonate concentration and comparison of salt removal with and without stirring is therefore important. Carbonate was therefore monitored using a Total Carbon (TOC) analyzer.

During the recent repairs of Igreja de S. Salvador, all tiles were removed to be applied again after restoration. The analysis of soluble salts present in mortars is important to find evidence for the several types of degradation factors that may be operating, and to advise actions to be undertaken to avoid future damage. Therefore, anions and cations removed from samples of mortars used for the application of tiles in Igreja de S. Salvador were also analyzed using the same techniques.

With the exception of a report mentioning the use of non-suppressed ion chromatography [2] in the determination of Cl^- , NO_3^- and SO_4^{2-} in the weathering crusts of a 13–15th century limestone cathedral in Mechelen, Belgium, to the authors best knowledge, ion chromatography and TOC analysis have never been used for this type of application before these studies were carried out [16–18], and they are shown to be extremely useful techniques for the identification and quantitative analysis of the salts removed.

2. Experimental

For desalination experiments tiles were immersed in 2000–4000 ml of deionized water (depending on their size) in closed glass or plastic containers, and salt removal was normally monitored for ≈ 1 month. No stirring was applied except before taking samples (7–15 ml) for analysis.

Conductometric measurements were directly made in the bulk of the immersion water with a Methrom Herisau E382 (Herisau, Switzerland) and an Ingold 109803000 cell (Urdorf, Switzerland). All conductivity measurements are reported at 20 °C. Whenever the temperature was different, the values were corrected using a factor of 2%/°C.

Measurements of pH were also made in the bulk of the immersion water. Normally pH values rapidly increased to 8.5–9.5 (in 5–10 h), then slowly

decreased to 7.6–8.3 (till ~200/300 h) and then stabilised without significant changes.

For analysis of soluble salts from mortars, 200 g of each sample, normally a thin powder, was mixed with 500 ml of deionized water in 700 ml bottles for 24 h with constant stirring. After this period stirring was stopped and a few minutes later ≈ 100 ml of the supernatant liquid was decanted.

The chromatograms were recorded with a Dionex 4000i ion chromatograph (Sunnyvale, CA, USA). Anions were analyzed using an Ionpac AG-4A precolumn, an Ionpac AS-4A column and an Anion MicroMembrane (AMMS-I) Suppressor; cations were analyzed using an Ionpac CG12A precolumn, an Ionpac CS12A column and a Cation MicroMembrane (CMMS-II) Suppressor. A Dionex conductivity detector and a Perkin-Elmer Nelson Model 1020 desktop integrator were also used. The volume introduced into the injection valve of the instrument was normally 1.5 ml and the loop volume was 50 μ l. Merck (Darmstadt, Germany) Anotop 10 filters (0.2 μ m–10 mm) were used to remove particles. For each sample at least two analyses were performed.

Carbonate and organic carbon was measured with a Dohrman, Rosemount Analytical High Temperature TOC Analyzer DC-190 (Santa Clara, CA, USA). For each sample, four 50 μ l injections were performed. This instrument was calibrated with standards of potassium hydrogenphthalate. The calibration curve is calculated automatically by the instrument and the results are given in ppm of C (carbon).

Deionized water was obtained from distilled water using a Millipore water purification system (Bedford, MA, USA).

As tiles and fragments of different shapes, sizes and masses, and different volumes of immersion water were used, the experimental results were normalised by dividing them by the factor: m/V , where V is the volume of immersion water (in l) and m is the weight (in g) of the tile or tile fragment, these units being chosen for practical reasons. For concentrations of ions in ppm, these normalised values give the concentration of the ions (in ppm) for 1 g of the tile immersed in 1 l of water. The same applies for conductivity assuming that this property varies linearly with the concentration of the ions present. This normalisation permits the comparison of results obtained in different experiments and the

approximations involved are suitable for the purpose of this work.

We used traditional reference methods for recording the position of the tiles. The several walls, columns, niches, altars and choir of Igreja de S. Salvador were divided in several parts and given letter/number codes. For each of these parts, a letter and a number corresponding to the horizontal and the vertical rows, respectively, was given to each tile according to their position. The tiles and mortars were carefully sampled in order to find evidence for the several types of degradation factors that could be operating and which appeared evident in some cases. Among these one can mention the action of rain, capillary rising from the ground, underlying water and from masonry walls, biological activity including excretion by macroorganisms (e.g. pigeons) and microorganisms (e.g. algae), and of unsuitable materials such as white cement or Portland cement used in repairs to which the tiles and walls were previously subjected.

3. Results and discussion

Several 18th century tiles from Igreja de S. Salvador (P8A5, P8A7, P8M6, P2AC32, P2AD32, P1G1 and P2J15) were studied. Fig. 1 shows an anion chromatogram for the P8A7 tile. In this case Cl^- , NO_2^- , NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ were detected. For the other tiles only Cl^- , NO_3^- and SO_4^{2-} were detected. Since tiles do not contain significant amounts of these anions in their composition, their presence must be due to salt infiltration into the ceramic body while the tiles were on the walls. Fig. 2 shows a cation chromatogram for the P1G1 tile.

The normalised conductivity of the immersion waters for tiles increases rapidly till ≈ 190 h (8th day) of immersion and shows a trend to level off after 2 weeks. Fig. 3A shows results for NO_3^- and Cl^- by suppressed IC and Fig. 3B shows results of SO_4^{2-} by ion chromatography, and carbonate using the TOC analyzer. For this tile, results for Cl^- are of the same order of magnitude and show the same trend as those of NO_3^- . However, the SO_4^{2-} concentrations are about 1/20 of those for Cl^- or NO_3^- , the time evolution has a less convex (i.e. more linear) appearance and does not stabilise after 850 h

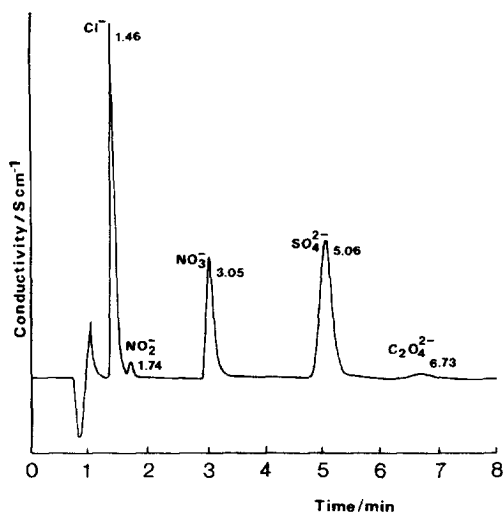


Fig. 1. Anion chromatogram obtained for a sample of the water of immersion of tile P8A7. Injection volume: 50 μ l; eluent: NaHCO_3 (0.75 mM) and Na_2CO_3 (2.2 mM); flow 2.0 ml min^{-1} . The numbers near individual peaks are retention times.

(35 days) of immersion. For carbonate after ≈ 500 h (~ 20 days) of immersion, an inflection towards an additional increase may be seen. These results indi-

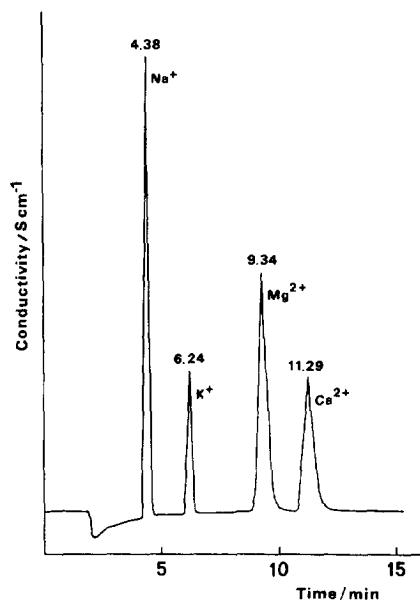


Fig. 2. Cation chromatogram obtained for a sample of the water of immersion of tile P1G1. Injection volume: 50 μ l; eluent: H_2SO_4 (11 mM); flow 1.0 ml min^{-1} . The numbers near individual peaks are retention times.

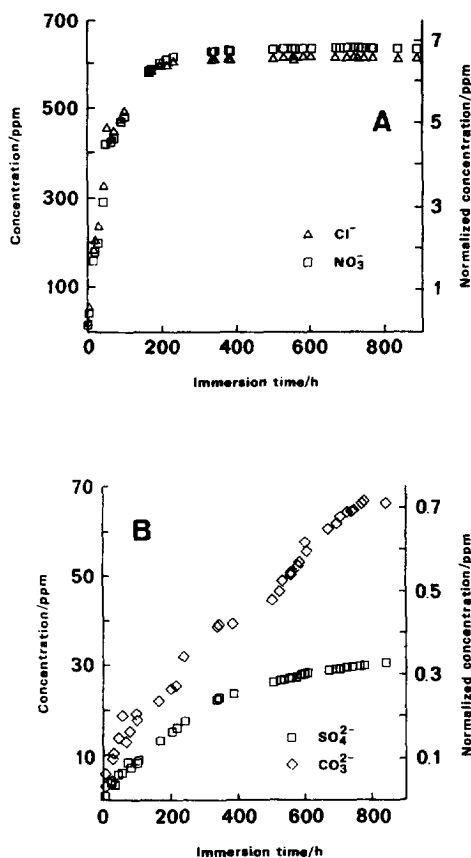


Fig. 3. Time evolution of anion concentrations (and normalised anion concentrations) in immersion waters of tile P2AD32. Cl^- , NO_3^- and SO_4^{2-} were analyzed by suppressed ion chromatography, and carbonate using a TOC analyzer (see text).

cate that the kinetics of salt removal depends on the anion involved.

For the P2AD32 tile NO_3^- and Cl^- are the main anions contributing to the conductivity; this is not the case for tiles P8A7 and P1G1. In fact for tile P1G1 after ≈ 100 h (4–5 days) the relative amount of the anions removed differs (Fig. 4): the concentration of nitrate is approximately twice the concentration of chloride and four times larger than the concentration of sulphate. For this tile the time evolution of nitrate and chloride concentrations in the immersion water is similar to the P2AD32 tile (Fig. 3A), but the evolution of sulphate concentration is different: there is a very fast increase of SO_4^{2-} concentration during the first 24 h. This also partly happens for Ca^{2+} concentration (Fig. 5). This could be due to an

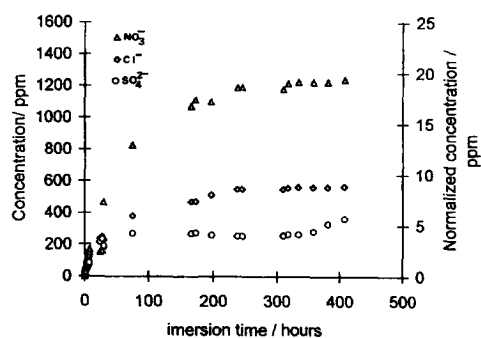


Fig. 4. Time evolution of anion concentrations (and normalised anion concentrations) in immersion waters of tile PIG1 as analyzed by suppressed ion chromatography. Carbonate was also analyzed using a TOC analyzer; its concentration increases slowly, with an inflexion at ≈ 170 h, but after ≈ 400 h (≈ 17 days) of immersion its concentration was only ≈ 6.5 ppm.

incomplete cleaning of the surface of the ceramic body; anions from residual mortar or grout were near the surface and can be quickly dissolved during the first period of immersion. The SO_4^{2-} normalised concentration then stabilises at around 4 ppm until

≈ 335 h (14th day) of immersion and increases again gradually to approximately 5.6 ppm until ≈ 400 h (17th day). After ≈ 335 h (14th day) of immersion, although the concentration of all four cations analyzed by ion chromatography increased gradually (Fig. 5), no significant relative increase is detected similar to the SO_4^{2-} case. The kinetics of removal of Na^+ and K^+ are approximately similar. The removal of Mg^{2+} , probably due to leaching of non-reacted dolomite or other Mg^{2+} -containing material as, for example, impure gehlenite, occurs with a slower kinetics but after ~ 200 h the Mg^{2+} and Ca^{2+} concentrations are of the same order of magnitude.

The mortar used in the application of tile PIG1 had a grey appearance and probably contains Portland cement. Mortars used for the other tiles studied had a white yellowish or brownish colour. This probably explains the much greater concentration of SO_4^{2-} found in desalination experiments for PIG1 tile as compared to P2AD32 (and others).

The relative amount of the anions (and cations) removed and the corresponding kinetics clearly depend on the position of the tiles on the walls, as the nature and amount of the soluble salts present depend on their origin, particularly if they were introduced through the roofs, by capillary rising, mortars, cement, etc. However, the evolution of the carbonate removal approximately displays the same trend in all cases analyzed, particularly the more or less noticeable inflexion of the curves after 17–20 days of immersion. This suggests that the existence of carbonate in immersion waters has a different origin from the other anions.

Carbonates are probably due to erosion of the ceramic body which contains a significant amount of carbonate materials (e.g. CaCO_3). The desalination experiments were done in closed containers which were only periodically opened for removal of samples for analysis. The carbonate concentrations are normally well below the solubility of CaCO_3 at pH 7.5–9.5; therefore, although one might expect a progressive dissolution of CO_2 and a corresponding dissolution of CaCO_3 to $\text{Ca}(\text{HCO}_3)_2$, this does not appear to be the dominant factor.

As an attempt to further identify the possible soluble salts precipitated in the pores of the ceramic body of the tiles, the immersion waters of the P2AC32 and P2AD32 tiles were evaporated and the

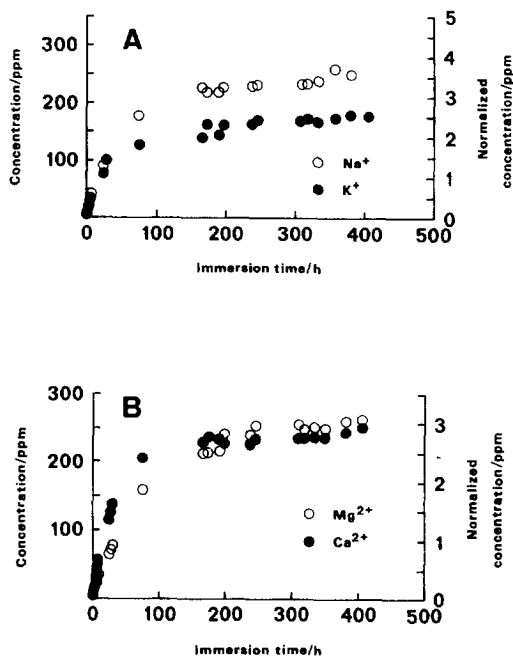


Fig. 5. Time evolution of cation concentrations (and normalised cation concentrations) in immersion waters of tile PIG1. The cation concentrations were determined by suppressed ion chromatography.

solid residue was examined by X-ray diffraction. KNO_3 and NaCl are clearly identified. However, no sulphate phase could be accessed.

With fragments from tile P2J15 we tried to evaluate the effect of desalination on the mineralogical constitution. The X-ray diffractograms ($\text{CuK}\alpha$ radiation) of the ceramic bodies before and after treatments with water–ethanol (99:1) or with water– H_2O_2 (130 vol.) (98:2), common immersion solutions used at Museu Nacional do Azulejo (National Tile Museum), showed that in the 2θ angular region of the XRD spectra the relative intensities of the hematite, gehlenite, dolomite, calcite, feldspar and quartz lines are the same. In this particular experiment we therefore conclude that no significant minerochemical or structural modifications occurred after immersion of the P2J15 tile. However, for the highly degraded tiles, particularly those in which the layers are very fragile or powdery, more or less obviously showing the risk of collapse of the body or detachment of the glaze, their immersion is obviously not recommended.

Most of the tiles from Igreja de S. Salvador are

rather friable, mechanically weak and apparently very prone to salt damage in part due to the possibility of ready transfer of salts through the large gaps and pores that exist between the layers. The salts may accumulate in these gaps and pores, at the glaze–body interface and even in the holes of the glaze. As these salts go through cycles of dehydration, rehydration and recrystallization, the deterioration of the tiles is unavoidable. Therefore, sources of soluble salts should be removed from the materials that surround the tiles applied on the walls.

After removing the tiles from the walls for restoration, it became clear that the nature of the mortars used varies significantly as some are the original ones (from the 18th century), and many others have been used in successive repairs till 30 years ago (e.g. Portland cement). Different mortars certainly produce different problems in the tiles and it was important to sort out what type of soluble salts were present in these. Table 1 shows results of analysis of anions and cations in samples of mortars removed from selected places of Igreja de S. Salvador during the restoration works that proceeded during 1995 and

Table 1

Concentration of anions and cations in the supernatant liquid of the mixtures: mortars/water (see text)

Sample	Conductivity (S/cm)	pH	Cl^- $\times 10^{-3}$ (ppm)	NO_2^- (ppm)	NO_3^- $\times 10^{-3}$ (ppm)	SO_4^{2-} $\times 10^{-3}$ (ppm)	$\text{C}_2\text{O}_4^{2-}$ (ppm)	CO_3^{2-} $\times 10^{-2}$ (ppm)	Na^+ $\times 10^{-2}$ (ppm)	K^+ $\times 10^{-2}$ (ppm)	Mg^{2+} $\times 10^{-3}$ (ppm)	Ca^{2+} $\times 10^{-3}$ (ppm)
1	8.42	8.61	1.52		3.28	1.38		0.40	6.08	4.53	0.77	0.09
2	4.85	8.17	0.79		2.08	0.02		0.42	3.27	3.45	0.37	0.93
3	8.00	8.63	1.57		2.81	0.05		0.49	6.11	4.68	0.59	0.11
4	13.01	8.95	2.13		6.33	0.05		0.45	8.94	8.06	1.40	0.19
5	0.36	9.72	0.03	0.37	0.05	0.01	1.99	0.11	0.27	0.17	0.03	0.01
6	8.08	8.75	1.72		3.11	0.02		0.43	6.32	5.17	0.58	0.19
7	0.41	9.54	0.03	0.48	0.08	0.02	8.48	0.09	0.29	0.08	0.05	0.02
8	12.4	8.96	2.86		3.90	0.57		0.99	13.88	9.85	0.77	0.19
9	0.56	10.12	0.03	0.84	0.12	0.01	0.98	0.11	0.31	0.28	0.05	0.01
10	12.12	8.57	2.29		5.61	0.16		0.84	11.54	9.71	1.05	0.33
11	3.72	8.63	0.61		1.52	0.01		0.41	1.99	3.54	0.28	0.12
12	7.14	7.94	1.13		3.54	0.05		0.33	4.85	4.89	0.46	0.34
13	8.51	8.84	1.72		2.69	1.04		0.36	9.67	8.85	0.61	0.30
14	8.99	8.43	1.17		5.39	0.14		0.29	6.66	7.01	0.70	0.43
15	0.49	7.93	0.02		0.03	0.03		0.03	0.69	0.35	0.05	0.05
16	3.96	8.4	0.24		3.55	0.03		0.24	3.38	1.04	0.46	0.44
17	11.43	7.84	1.37		6.02	0.03		0.48	6.75	8.91	1.52	0.48
18	11.43	7.56	0.90		8.59	0.02		0.54	3.84	5.71	1.41	1.48
19	6.25	7.67	0.25		4.17	0.02		0.80	1.86	1.05	0.52	1.57
20	8.16	7.58	0.38		5.37	0.01		0.63	1.95	2.58	1.00	1.38
21	7.84	7.89	0.33		4.99	0.02		0.48	1.96	1.93	0.82	1.35
22	6.25	7.72	0.20		3.28	0.02		0.73	1.62	1.55	0.64	1.25

1996. This table shows that depending on their positions on the walls of the church, mortars, and, consequently, the ceramic bodies of the corresponding tiles, have very different amounts and natures of soluble salts.

The results shown in Table 1 proved to be very important and the architect responsible for the restoration works was therefore able to plan what sort of actions should be undertaken to avoid future damage after the application of the tiles. For the tiles and mortars the presence of Cl^- and NO_3^- is probably due to the permanent existence of hundreds of pigeons on the roofs. There are reports of serious infiltration of rain water due to very damaged roofs approximately 40 years ago, and even recently, when visiting the church before the present restoration works, the walls were humid and salts containing Cl^- and NO_3^- could be easily seen covering many tiles. In some places near the ground, however, there is (or was) underlying water and/or sewage flowing and the mortars and masonry walls had a green appearance and very high NO_3^- concentrations were detected as well as high levels of organic carbon.

4. Conclusion

The implementation of ion chromatography techniques to monitor the removal of soluble salts appears to be a promising procedure in old ceramics (and other materials) preservation studies. The possibility of using this chromatographic method as a practical procedure for monitoring salt removal, or as a convenient procedure for the identification of the ions present in the materials that surround the tiles applied on the walls seems very promising. The next step is to find the safest and most efficient methodologies of reducing the high salt contents often found to lower, more stable levels without further deterioration of the tiles. A variety of soaking techniques commonly used in conservation, and modifications of these, can now be tested against one another for effectiveness. These studies are in progress.

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