Use of poulticing in desalination of masonry units – implications on salt-deteriorated structures

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Cellulose poulticing is a widespread method of desalination in practice for removal of salts from ancient structures. Optimization of the process is essential, considering that poulticing/desalination is the prime step during the protection of existing structures in the coastal zones. Even though poulticing is widely used in European countries, it is not common in India, because the principle and efficacy of the method have not been studied so far for masonry materials in the ancient Indian structures with specific microstructure. The present study analyses the effect of cellulose poulticing in bricks considering the role of pore size in the substrates and the removal of different types of salts depending upon the pore distribution. The process was found around 74% more efficient in removing Na2SO4 than NaCl in materials with more micropores (pore size <1 μm), as demonstrated from scanning electron microscopy images and analysis of pore structure using mercury intrusion porosimetry on brick samples. Interesting results on the unsuitability of cellulose poulticing in certain materials and the reasons for the same were obtained, which are based on the predominant transport mechanisms for salt removal. The study would be a reference for initiating cellulose poulticing as an effective desalination method in the ancient structures of coastal southern India.

Keywords: Conservation, desalination, historic structures, protection, salt weathering.

SALT-INDUCED degeneration is recognized as one of the most crucial causes of damage for masonry structures1-3. Salts introduced into the materials from external exposure can cause crystallization inside the material microstructure owing to changes in temperature and humidity, and also depending upon the nature of the salt. Repetitive dry–wet cycling increases the concentration of salts inside the pores, causing them to get supersaturated and inducing crystallization pressure on the pore wall, thus damaging the material. Hence, periodical removal of salts (desalination) is essential from porous masonry to prevent deterioration, and is also a must pre-repair/protective strategy while dealing with salt-deteriorated structures using various treatments. Desalination techniques have not been explored significantly in India, despite the ease of applicability and their economic sustainability.

Background

Different desalination methods proposed/in use are broadly listed as diffusion (baths)4, electro-migration, vacuum/water pressure extraction, utilizing barium compounds to insolubilize the salts by intervening at room temperature5-7 and methods that involve microbiological reactions or microwave ovens8. Among these, immersion in water is a generally accepted method for desalination in laboratory studies, but it is impractical for the existing structures. The use of absorbent poultices is one of the most commonly used and an easily adaptable salt-removal techniques for the existing structures. Another solution to the problem of salt-removal is the application of products modifying crystallization kinetics. It is reported that such modifiers can alter the supersaturation and permit migration of salts to the surface, by affecting the evaporation rate9. For the transport of salts in fine porous materials where other techniques fail, electrochemical chloride extraction can be adopted. However, electrical resistance of the material and the varying tortuosity inside the pore system can adversely affect its efficiency, by causing an inhomogeneous flow of current inside a highly layered and tortuous material structure10.

Poulticing is considered as the most suitable method of salt removal from existing structures11,12. A better understanding of the process with various desalination methods would provide guidelines for engineers and conservators to efficiently select the poultice material according to the existing exposure condition at the site and the substrate material. The efficacy of the process depends on the transport phenomena in the material, which are determined by pore structure and pore size distribution. The capillary suction provided by the cellulose poultice to the substrate clearly depends on the size of the pores in the substrate12,13. Nuclear magnetic resonance has been used in laboratory experiments to document the performance of various
poultices in contact with common substrates, and has demonstrated that the pore size of the substrate must be in proportion to that of the poultice for efficient desalination12. Different poulticing materials that have been tested in the past include clay, cellulose, minerals like diatomite, fume silica, rock wool and sacrificial mortars in the form of lime – among which clay and cellulose are the most frequently used4,15,16. Although clay is appreciated for its good adhesion with the substrate, difficulty to cleanly remove it makes its use restricted to objects without any heritage value17. Cellulose poulticing is practised well in the Western countries and has demonstrated effectiveness in removing moisture as well as salt from structures, especially with high efficacy for brick masonry18. Cellulose compounds are easy to work with, have neutral pH, high plasticity and water absorption, although the adhesiveness is poor (compared to clay) in vertical applications. Hydrophilic mineral wool has been studied for its potential to be utilized for poulticing in masonry materials as an alternative to cellulose, considering its advantages such as faster transport of moisture and salt, repetitive usage, etc.19. However, it could be used only for water transport (keeping the wool dry) or salt transport (keeping the wool saturated) at a given time.

Optimizing the efficiency of poulticing in a particular material by designing the poultice with new materials has been reported by Lubelli and Hees11. Besides the pore structure of the substrate, the mechanism of advection by the poultice can differ largely based on the kind of salt to be removed. The mechanism of salt deposition and further crystallization differs for each salt based on the chemical characteristics20–23. Kumar and Singh12 have reported the difficulties encountered in the removal of salts from the Mahabalipuram Shore Temple in Tamil Nadu, which is made of granite12. Optimizing such situations requires experimental studies revealing the performance of poulticing and its variation with respect to the controlling factors.

**Research significance**

The increasing risk of salt deterioration to historic structures due to the changing climatic conditions and floods has been reported worldwide20. Even though flooding is a short-term exposure of salt loads, the resulting dry–wet cycles in the affected structures stay active for several years and can even activate deep-accumulated salts within the materials from various past sources. Recent studies from Europe show that desalination is the most suitable conservation technique, among which poulticing is found as a promising and convenient method for immobile objects – related to heritage, including historic buildings. However, the transport mechanisms in poulticing systems are not experimentally reported, which is crucial in evaluating the effectiveness and performance of such methods. Despite its common application in architectural conservation, the method has produced questionable results with different types of poultices, salts and substrates4,15. No studies are reported to define the variability in the efficiency of cellulose poulticing depending upon the combination of substrate microstructure and type of salt. The present study addresses this issue, by experimentally analysing the comparative efficacy of cellulose poulticing in masonry and correlating it to the possible transport mechanisms through microanalytical techniques – using bricks of different microstructures exposed to different salts.

The present study examines the effect of cellulose poulticing in bricks considering factors such as different pore sizes in substrates and removal of various salts. Sodium sulphate and sodium chloride are the salts considered in this study. Sodium sulphate is the most deleterious salt causing degeneration in masonry materials, especially in these with pores less than 1 μm (refs 23, 25). Sodium chloride was studied, considering the fact that most of the affected structures in India lie in the coastal zone where this is the major prevailing salt, even though the damage due to sodium chloride to the material is much lower compared to that of sodium sulphate with respect to salt crystallization26.

**Materials and methods**

**Properties of samples used**

Since pore structure is a critical material property that affects the process of poultice desalination, two types of fired clay bricks depending upon their difference in pore structure were selected for the study, which are commercially available and sourced from Chennai, TN. The first type of brick sample was denoted as HP – a ‘high porosity’ brick, with large pores and low density. The second type was denoted in the study as LP – a ‘low porosity’ brick with more micropores and high density. Next, 40 mm cube specimens were made using both brick types (by removing the external exposed surfaces with irregularities from all sides), each with variants of uncoated and coated with two different types of protective coatings – one a silicone-based water-repellent (SC), and the other an acrylic–siloxane based water-repellent (AS). These were reported to have entirely different mechanisms of action in a previous study by Monahar et al.23. The cubes were cut out of the whole bricks using a diamond blade cutting machine, and with water as a coolant to minimize crack formation during the process of cutting. The samples for the tests were thus denoted as HP, HP–SC, HP–AS, LP, LP–SC and LP–AS, where SC and AC represent two different types of water-repellent coatings. Three replicates of each variant of the specimens were used for all the tests. Table 1 gives the physico-mechanical and pore-structure characteristics of the two brick types (HP and
Compressive strength (MPa) 8.1 12.3

Water absorption (%) 18.4 10.3

Ultrasonic pulse velocity (m/s) 1400 1950

Table 1. Physico-mechanical and pore structure properties of the samples

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>High porosity (HP) brick</th>
<th>Low porosity (LP) brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions (mm)</td>
<td>220 × 110 × 30</td>
<td>220 × 110 × 50</td>
</tr>
<tr>
<td>Image</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>8.1</td>
<td>12.3</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>1.65</td>
<td>2.10</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>18.4</td>
<td>10.3</td>
</tr>
<tr>
<td>Ultrasonic pulse velocity (m/s)</td>
<td>1400</td>
<td>1950</td>
</tr>
<tr>
<td>Porosity (% from Mercury)</td>
<td>49</td>
<td>31</td>
</tr>
<tr>
<td>Intrusion Porosimetry (MIP)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical pore size (µm from MIP)</td>
<td>11.1</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Results and discussion

Samples were subjected to accelerated salt crystallization weathering according to RILEM Test no. V 1.1b, 1980 for 112 consecutive dry–wet cycles with both sodium sulphate and sodium chloride salts separately. Table 2 provides details of the weathering test methodology followed. The different degrees of damage and different amounts of salt inside the samples were because of the pore size distribution of each sample.\textsuperscript{10,11} Poulticing with cellulose pulp was applied on all the weathered samples to remove the salts, and the effect of desalination was examined using microanalytical tests like SEM (for qualitative and visual analysis) and MIP (for quantitative analysis).
Table 2. Details of the accelerated weathering test adopted

<table>
<thead>
<tr>
<th>Solution concentration</th>
<th>For sulphate weathering test: 10% Na₂SO₄ anhydrite solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For chloride weathering test: 15.6% NaCl solution</td>
</tr>
<tr>
<td>Duration of one cycle</td>
<td>24 h : 2 h immersion, 19 h drying at 60°C, 3 h room cooling (~27°C)</td>
</tr>
<tr>
<td>Sample size</td>
<td>40 mm cubes</td>
</tr>
</tbody>
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Scanning electron microscopy

The effect of desalination on weathered samples was examined by capturing SEM images on samples before and after desalination. Cellulose poulticing was found to be effective in removing salts from the pores, for both sodium sulphate and sodium chloride salts (Figures 2–4).

Figure 2 shows the interior of a weathered (with Na₂SO₄ exposure) LP–SC sample after desalination (sample was taken at a depth of 3–5 mm from the surface). Larger pores that opened up without any salts in them are observed in this figure. This is indicative of the efficiency of cellulose poulticing in removing sodium sulphate salt from the bricks. EDS spectrum was collected at the open pore observed in the SEM image and is also shown in Figure 2. Sulphur is not shown in the spectrum, which is indicative of the absence of sodium sulphate in the pores. Poullicing was also applied on samples subjected to NaCl weathering. Figure 3 shows the surface of a weathered sample (HP) with NaCl exposure, before and after desalination. EDS spectrum of the whole area of the SEM image in Figure 3 also shows the absence of NaCl in the surface from the mineral composition. The weathered surface before desalination (Figure 3) clearly exhibits larger NaCl crystals, almost completely covering the exposed area. The image of the sample surface after desalination shows that the NaCl crystals have been completely removed from the surface. In addition, new small pores have opened up from which salts would have possibly been removed. Figure 4 shows SEM images taken on desalinated samples collected 3–5 mm deep from the surface of a weathered, uncoated LP sample (with NaCl). The large group of micropores observed shows that NaCl could deposit in pores of such small size, and poulticing could remove NaCl salts even from these small pores. However, SEM images are insufficient to quantify the efficiency of complete removal of salts.

Porosity measurements

With the assurance that cellulose poulticing practically works for both Na₂SO₄ and NaCl salts, MIP was used in the desalinated samples to identify the actual pore structure and pore distribution on weathering, excluding the effect of possible salt deposition.

Total porosities were measured for each specimen – before weathering, after accelerated weathering and after desalination of accelerated weathered specimens, using MIP on samples collected 20 mm from the surface. Porosity changes were calculated using the data from MIP tests conducted on the same samples corresponding to before weathering, after weathering and after desalination stages. The porosity values were then compared for each type of brick exposed to various salt solutions (Na₂SO₄ and NaCl) to compare the efficiency of cellulose poulticing to remove salts (Figure 5). Comparing the change in porosities on desalination among sulphate weathered samples and chloride weathered samples, a general observation that can be made is that cellulose poulticing is evidently more efficient in removing sodium sulphate than sodium chloride salts from the LP bricks. Due to the greater occurrence of macropores in the case of HP samples, sodium sulphate salt crystallization and deposition is not highly favoured. The reason is the dissolution-mediated phase transformation of sodium sulphate to reach supersaturation in smaller pores. This process occurs because of the transitions between the two significant stable phases of sodium sulphate, viz. thenardite (Na₂SO₄) and mirabilite (Na₂SO₄⋅10H₂O). Thenardite to mirabilite conversion...
occurs by the process of dissolution and recrystallization. As the relative humidity decreases and evaporation rate increases, an increase in the relative proportion of thenardite is observed. At equilibrium, thenardite is not expected to crystallize at temperatures less than 32.4°C, but it occurs only at non-equilibrium condition in most porous materials. Below 32.4°C, mirabilite (Na₂SO₄⋅10H₂O) is the stable phase. Mirabilite rapidly dehydrates at a relative humidity (RH) below 71% (20°C) to form thenardite. Also, thenardite will rehydrate to mirabilite when the...
humidity exceeds 71%. So, a solution that is unsaturated with respect to thenardite may already be highly supersaturated with respect to mirabilite. Figure 6 shows the X-ray diffractogram of a brick affected by sodium sulphate (specimen LP is shown), in which simultaneous presence of mirabilite and thenardite can be observed. This discussion provides clarity on the severity of damages associated with sodium sulphate salt. In the present case, this is evident from the observation of the negligible difference in total porosity values before and after desalination in HP, HP–SC and HP–AS samples (Figure 5a). LP, with its inherent micropores and newly formed micro-fissures on weathering, facilitates easy crystallization and precipitation of sodium sulphate salts, which are then removed on desalination. Whereas, the difference between total porosity before and after desalination in case of chloride-affected samples is much higher (Figure 5b). This is because NaCl salt does not encounter phase transitions, but gets precipitated and deposited on evaporation. Hence, a remarkable number of macropores in HP would get filled with NaCl salts. The accumulated NaCl salts from HP are then removed on desalination resulting in an increase of up to 13% total porosity.

In the case of LP, the exposure of sodium chloride solution results in the deposition of NaCl crystals in the larger portion of micropores which are abundant in the LP system. Smaller ionic size and easy mobility of NaCl aid its deposition in the micropores. Much higher capillary action is required to remove these salts from the micropores – which would result in a decreased efficiency of desalination in LP bricks affected by NaCl. No difference in the trend was observed for samples applied with the water-repellents in all the cases; the reason could be their sacrificial behaviour during the accelerated salt crystallization tests.

Figure 7 shows the differential intrusion curves for samples at different conditions using the corresponding data derived from the MIP test. The peak of each differential intrusion curve represents the critical pore size of the sample, which is the pore diameter corresponding to the maximum mercury intrusion, or it is similar to the most common pore size in the material. Figure 7a shows the differential intrusion curves for HP, where the nomenclature for reading the plots is as follows: HP is the curve corresponding to unweathered form of the HP sample, HP Cl is that for HP weathered with chloride salt, HP Cl-de is the desalinated form of HP Cl. A similar nomenclature is followed for the LP brick (Figure 7b). The upward shift of curves in the pre-peak region denotes salt deposition in the pores of that region. The reversal of this upward shift denotes the removal of salts from the pores. It can be seen from Figure 7a that the critical pore size does not significantly change in the HP brick, before and after weathering or desalination. This is because of the inherent high salt weathering resistance of the HP brick due to larger pores in which salt damage is minimum. Salt deposition in the case of HP is evident with chloride and sulphate salts inside the pores, along with the effective removal of these salts (dotted lines), because of the ease of removal from the large pores. In the case of LP, salt deposition is higher for sodium chloride (which can be seen from the larger area under the curve prior to peak); however, the corresponding salt removal is not significant, because of the failure of capillary suction to transport salts from such small size, when the pore sizes in the poultice are larger than that of bricks. However, removal of the precipitated sodium sulphate salts is more prominent in the case of LP. This is because sodium
sulphate gets deposited in the larger pores in the brick matrix (larger than that of the pores in cellulose poultice). These observations are in support of the inferences from quantitative porosity analysis.

Figure 8 is a schematic representation of the matrix of HP and LP bricks with large pores and micropores respectively, where selective deposition of sodium sulphate and sodium chloride crystals is shown. The figure is not drawn to scale. Figure 8a and b illustrates the sodium sulphate crystals being deposited in large pores of HP and small pores of LP respectively. In HP, the crystals do not encounter any growth restraint; they are in equilibrium and do not cause any crystallization pressure on the pore walls. In LP, there are smaller pores of different size ranges. Sodium sulphate crystallizes and induces crystallization pressure on pores of size between 0.2 and 1 μm predominantly in such types of microporous brick material23,26. Pores smaller than 0.2 μm are difficult to access for sodium sulphate crystals to get precipitated. Thus, in Figure 8b, pores smaller than 0.2 μm remain empty, but salt crystals are seen in the other pores. Figure 8c and d shows the cases of HP and LP with NaCl precipitation in the pores. In Figure 8d, because of the small ionic size and high mobility associated with NaCl, the salt can get precipitated even in pores of size 0.01 μm (refs 11, 23). However, the capillary force induced by the cellulose poultice due to correlation between pore size distribution of the bricks and cellulose facilitates only salt absorption from pores larger than a particular size5. Hence, in Figure 8d, NaCl crystals do not get removed from some of the pores of LP which are difficult in considering the limited ability of cellulose poultice to induce capillary suction, thus decreasing the efficiency of the desalination process. This could be the possible reason for reduced desalination efficiency in removing NaCl from microporous material (LP) observed in the porosity quantification study (Figure 5b).

The movement of salts can generally occur by the action of diffusion where the ions move owing to the difference in concentrations gradient between nearby areas (using the principle of Fick’s laws), and advection where ions move in the direction of flow of water27. Diffusion is the more natural process which has been prominent in the present study, between cellulose poultice and the bricks considered (LP and HP). Advection could be predominant in case of poulticing, because of the moisture state and condition of substrate involved in the process. During the drying phase, when the water evaporates, salt can move along with the liquid and take advantage of the transport direction. Advection is a faster process; however, poultices should be specially designed with smaller pore size than that of the substrate for facilitating the advective component11. The present study suggests that normal cellulose poulticing is not efficient in removing NaCl from the small pores available in microporous dense materials like LP bricks here. So advection may be further studied by adopting mix composition for cellulose with materials such as sand, kaoline, etc. that forms a pore structure denser than that of LP. If the poultice has a capillary pressure greater than that in the substrate, during the poultice drying, advection will govern to extract the salts14,28,29. Even when the Washburn’s equation establishing the indirect relationship between pore size and capillary force is valid, it is convenient that the pores in the poultice are not extremely small which slows down the process of salt transport. Hence, the present study demonstrates the importance of choosing the cellulose poultice material based on the type of salt and pore structure of the substrate unit.

Considering the convenience and ease of using the poulticing technique for desalination, the results from this study can be used to optimize the choice of poulticing to any construction material such as concrete or any kind of stone depending upon their pore structure and the type of salt to which the structure is exposed. The texture of different materials inside the pores may have an influence on the capillary action, which has not been examined in this study. Any masonry material with a microporous structure such as granite (normally with a critical pore
size around 0.01 μm) or concrete (with normal OPC or with blended cements typically has a critical pore size around 0.1 μm) can have NaCl deposition in the micropores if exposed to salt. NaCl is difficult to remove by cellulose poulticing from the very fine micropores because of the high surface tension of the molecules and the requirement of very high capillary force. Whereas sulphate exposure can deposit salts only in the available larger pores, which can be easily and effectively removed by cellulose poulticing. Hence the method is recommended for desalination in such materials (microporous) only if the exposure is predominantly to sodium sulphate – which is the most deleterious salt. However, in the case of materials with a large proportion of pores of size greater than 1 μm, such as volcanic rocks (basalt, pumice stone), coral stones, perforated or air-entrained concrete, etc. either chloride or sulphate salts would be precipitated in the large pores, and these can be effectively removed using the cellulose poulticing technique. For microporous materials such as granite or microporous bricks in the coastal areas, future studies are needed on desalination techniques like electromigration or poulticing combined with electromigration.

**Conclusion**

- SEM images show that cellulose poulticing is effective in removing both sodium sulphate and sodium chloride salts from the surface of any material. The requirement of capillary force by the poultice to deploy the suction of salts is relevant only for the interior of the material where salts deposit inside the pores.
- On comparing the efficacy quantitatively by evaluating the total porosity using MIP on salt-weathered samples before and after poulticing at the interior (depth of 20 mm from the surface), it was found that the process of desalination was around 74% more efficient in removing sodium sulphate than sodium chloride salt, in materials with more micropores (pore size <1 μm). This is applicable in the case of any material irrespective of its chemical nature, e.g. bricks, stones (granite), concrete or mortar that satisfies the prescribed pore size ranges.
- If the material is mostly comprised of macropores (pore size >1 μm), desalination by cellulose poulticing is equally efficient to remove sulphate and chloride salts. This is valid for materials such as coral stone,
volcanic stones like basalt, laterite, lightweight concrete, etc.

- The present study shows the inefficiency of cellulose poulticing for the complete removal of NaCl salts from a more microporous system, where other advanced methods like advection by designing a poultice with finer pore system or electrokinetic desalination with migration component may be adopted.

Conflict of interest: None.


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