A. Elena Charola* and Christine Bläuer

Salts in Masonry: An Overview of the Problem

DOI 10.1515/rbm-2015-1005

Abstract: One of the key deterioration factors for porous inorganic building materials are soluble salts. To be able to remediate or mitigate this problem it is fundamental to understand the principal processes governing their behavior. While the actual mechanisms involved in these processes are still under study, the deterioration can be mitigated or remediated by the long practical experience gained in the field. The paper aims to provide an overview of the basic principles that rule the interaction of salts with the porous inorganic material. Understanding these will allow the development of appropriate procedures to control the deterioration process.

Keywords: soluble salts, deterioration, porous inorganic materials, crystallization, hygroscopicity, deliquescence, clay interaction

1 Introduction

Soluble salts have long been recognized as one of the most important and generalized deterioration factors to affect inorganic porous building materials contaminated with them. During the past few decades, the significant number of studies carried out advanced the understanding of specific issues related to salt deterioration. However, the subject is very complex as deterioration depends not only on the salt system present but on the object itself and its environment. Therefore remediation or mitigation of salt weathering is a major challenge in each specific case. Nonetheless, many of the problems caused by salts can be approached and mitigated at a practical level once the key processes underlying salt crystallization are understood.

The present paper aims to give an overview of the current knowledge on salt deterioration in porous building materials such as stone, brick and mortar. Understanding the basic principles that govern the deterioration should help in recognizing the main issues governing each specific case so that the best approach to mitigate the problem can be identified.

*Corresponding author: A. Elena Charola, Smithsonian Institution – Museum Conservation Institute, 4710 Silver Hill Road, Suitland, MD 20746–2863, USA, E-mail: charola_ae@yahoo.com
Christine Bläuer, Mineralogist/Conservation Scientist, Conservations Science Consulting Sàrl, Route de Beaumont 13, 1700 Fribourg, Switzerland, E-mail: blaeuer@conservation-science.ch

2 Background information

There is a vast literature addressing this topic and several reviews have already been published [1–3]. Furthermore, international conferences have addressed specifically this topic [4–8] or included in a broader frame, such as mural paintings [9] or from studies carried out under European projects, such as the one on the Suomenlinna Fortress in Helsinki [10]; while journals have devoted specific issues to this topic [11, 12] and a webpage is dedicated to the subject [13].

There have been many advances in understanding the conditions required for the crystallization of salts, and particularly in the case of salt mixtures. The advances in computer programs have allowed developing expert models [14], such as Runsalt [15] that can calculate, for a given solution of mixed ions at specific concentrations, the order of precipitation of the various salts that can result at a given temperature and relative humidity. These programs consider solutions under equilibrium conditions, which are not necessarily those that occur in a porous body, but the knowledge of the theoretical pathway followed in the crystallization process is an enormous advance to understand the crystallization process.

On the other hand, technological advances have allowed following in-situ crystallization processes with changes of temperature and relative humidity – including laboratory studies, providing an actual evaluation of the visible crystallization process that result from thermohyg-ric changes [16, 17].

3 Salt presence in buildings

3.1 Condition survey and documentation

A condition survey is required prior to any major conservation intervention and it is usually during this process that the presence of salts is suspected either because salt efflorescence can be seen right away or deterioration patterns often associated with salts are observed (Figure 1).

However salt damage will not only present different morphologies on the various materials but these are also dependent on the environmental conditions (Figure 2).
Therefore external influences that affect the building and its materials should also be assessed and recorded. It is important to note both macro environment, such as general climate and particular weather at the time of examination, and micro-environment, e.g., whether the area is shaded by buildings or trees, protected from direct rain, etc. (Figure 3). In the case of interior environments, the average room climate, its relative humidity and temperature and their variation and variation frequency are the main parameters that need to be considered [18].

Documentation during condition survey is fundamental. This aims to bring together all the facts about the materials present, the environmental conditions and any other factors that can help explain the current condition of the building [19]. Only a thorough diagnosis will allow determining the causes and active mechanisms present in the building and its materials. This information is fundamental in devising the manner of addressing these problems in an effective and durable manner [20].

The documentation process – described in detail in various publications [21, 22], is fundamental for any diagnosis and subsequent considered intervention as well as for future reference. It is during the documentation process that samples should be taken and some properties of the materials be measured in situ. Among these, the water uptake rate, as with a simple drop of water [23], the RILEM tube [24] or the newly developed contact sponge method [25, 26], can help distinguish between

Figure 1: Typical weathering patterns caused by salts (granular disintegration and alveolization) on sandstone at the portal of St. Magnus Cathedral, Kirkwall, Orkneys.

Figure 2: Left: Sodium sulfate crystallizing at the subsurface in brick masonry causing the detachment of the flake that is being held showing the salt present also on its underside. Right: Portal at the Manhattan College in New York City, where this occurred. Figure 3 provides further information about this damage.
untreated materials or those treated with a water repel-

lent; salts can be distinguished from similar looking bio-

logical growth by the solubility in a drop of water for the

former, or the burning potential of the latter; alkaline

salts can easily be recognized by dipping a wet pH-test-

ing strip into them [27]. Furthermore, some salt analysis

can be done directly on site, such as spot tests or the use

of ion selective strips on efflorescence that reveal the type

of anions present. However, salt efflorescence only

reflects part of the salt system and, furthermore, they

undergo seasonal changes. To be able to understand the

source and distribution of the salt in a specific masonry

wall, samples need to be taken from the masonry at

different heights and depths and analyzed quantitatively

for both anions and cations [28–30]. But since the dis-

tribution of the salts changes over time, all sampling has

to be done on one specific day to be able to compare the

obtained results.

3.2 Origin of the salts

Salts present in building materials can originate from
different sources [31]. Some may be inherent to the
stone itself, as is the case of those deposited in a marine
environment. Man-made materials may also contain
them; for example, Portland cement may release impor-
tant quantities of sodium and potassium hydroxides,
sulfates and carbonates [32] while the binder of dolomitic
lime mortars may release magnesium hydroxide, carbo-

date and hydrogen carbonate [33], and bricks, if

not appropriately fired, contain sodium sulfate (see

Figures 2–3), all of which are water soluble [34].

However, significant amounts of non-autochthonous
salts can enter these porous inorganic materials once
they are part of a building or structure as a result of
water infiltrations such as rising damp, i.e., water rising
through the salt containing soil in contact with the wall
masonry so that salts accumulate in it over time, as is the
case in many churches that had the cemetery right next
to them. Buildings may also have been used to keep salts
in storage, such as common table salt, as in the crypt of
St. Maria im Kapitol in Cologne [35] and the smoke-house
in Colonial Williamsburg [36]; or gun powder containing
potassium nitrate. Or part of the structure may have been
turned to stables for cattle or horses, so that the nitrates
and sulfates of their manure would accumulate in the
walls. Similarly, latrines, or “garderobes”, in medieval
castles were directly attached to the outer walls, while
poorly constructed sewers discharged their content
near the structures, or if they had leaks, directly into
the walls.
When structures are on a flood-plain, as is the case of many Egyptian monuments close to the Nile, then salts from the river will accumulate in them, while buildings near the sea shore are subjected to salt spray [37]. In urban environment, air pollution will give rise to the formation of sulfates [38] that are mostly seen as gypsum crusts or magnesium sulfate efflorescence [39]. Table salt was traditionally used as herbicide to control weeds around buildings contributing to its introduction into the building material. In historic times, this practice was used to prevent enemy grounds from flourishing. In colder climate, the use of de-icing salts, mostly sodium or calcium chloride, results in significant damage to the materials [40].

Soluble salts may actually result from their interaction with materials in the building. For example, dolomite present in the stone will react with soluble sulfates originating from air pollution to form calcite and magnesium sulfate [41] where similar reactions with limestone or lime binders will produce gypsum. Also inappropriately applied conservation treatments may be responsible for introducing soluble salts. In particular, the cleaning of brick using an alkali wash followed by an acidic rinse can result in the introduction of significant amounts of salt, mostly sodium chloride if hydrochloric acid was used, and if the final rinse was not carefully carried out (Figure 4). The use of other acids, such as phosphoric or formic, will result in the corresponding salts being formed [42]. Last but not least, it has been found that in new construction gypsum efflorescence develop apparently because of the admixtures added to commercial mortar formulations such as air-entrainers, plasticizers and surfactants, the latter being probably responsible for the change observed in the crystallization of this salt [43].

3.3 Diagnosis of salt presence

Periodic observation of the building’s salt contaminated areas under different conditions, i.e., rain, dry spell, humid days, can give in many cases the key to design preventive conservation measures, and is, in many cases, far more effective than mathematical modeling. Because if it can be observed that a certain salt system regularly crystallizes when certain conditions are prevailing for a certain amount of time, this means unambiguously that these conditions should be avoided as illustrated by the case study reported by Arnold et al. [44]. However this is valid only in the case the salt system does not change. For example, if a salt reduction treatment is carried out the resulting “new” salt system will behave differently and will make new observations necessary [45, 46]. For a thorough discussion of this topic see Steiger et al. [28–30].

The following key observations should be taken into account when salts are suspected to be the deterioration factor and considering that the accumulation of salt in materials has occurred over the building’s life span, which for historic structures can be many centuries:
- Efflorescences are an indicator that salts are present in the building.
- On very humid days, efflorescences may not be visible, but the building may show “damp” areas at different heights, caused by the presence of hygroscopic salts.

Figure 4: On the fence surrounding the Silverman Hall Law Building of the University of Pennsylvania, efflorescence began to appear one year after its cleaning (1999) and continued to increase with each passing year. While the cleaning products were properly washed off from the building itself where no salt deterioration occurred, this careful procedure was not applied for the fence (Photo January 2005). Efflorescences are visible during the dry winters, while in the humid summers, these areas appear damp.
When salts are present, the observed damage is usually the result of repeated salt crystallization cycles.

4 Salt deterioration processes

The mechanism that induces salt deterioration has been much discussed. Two main theories were originally proposed, that of the development of a crystallization pressure, either by hydrostatic pressure or linear growth [47–49], and that of a hydration pressure [50]. Recent studies have shown that crystallization pressure can be calculated more accurately if the non-ideal behavior of saturated solutions is taken into account [51, 52] and it is made clear that for coarse pore stones, the development of a crystallization pressure is the result of non-equilibrium conditions these being the normal conditions found in real life situations.

The following sections address different interacting processes in more detail.

4.1 Salt crystallization basics

To understand the damage originated by soluble salts – salts having higher solubilities than gypsum – in porous building materials it is necessary to consider the key points that rule their behavior. These can be summarized as follows:

- Each salt has a specific solubility in water, i.e., the maximum amount of salt that can be present in a given volume of water.
- If more than one salt is present, their respective solubilities will be affected to a major or minor degree. In general, if the two salts have an ion in common, for example, Na₂SO₄ and NaCl, their solubilities will decrease. If they do not have a common ion, the solubility of the less soluble will increase, e.g., gypsum (CaSO₄·2H₂O) solubility increases in a NaCl solution (see Table 1).
- When water evaporates from a salt solution, its concentration will increase until saturation is reached. As water continues to evaporate, salts will crystallize out. This applies to both simple salts, such as sodium chloride, and hydrating salts, such as sodium sulfate, that can crystallize as an anhydrate, thenardite, (Na₂SO₄), or as a decahydrate (Na₂SO₄·10H₂O), depending on the temperature.

<table>
<thead>
<tr>
<th>Salt system</th>
<th>NaCl</th>
<th>Na₂SO₄</th>
<th>CaSO₄·2H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>6.1 mol/kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td></td>
<td>2.4 mol/kg</td>
<td></td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td></td>
<td>0.01 mol/kg</td>
<td></td>
</tr>
<tr>
<td>NaCl-Na₂SO₄</td>
<td>5.6 mol/kg</td>
<td>0.6 mol/kg</td>
<td></td>
</tr>
<tr>
<td>NaCl-CaSO₄·2H₂O</td>
<td>6.2 mol/kg</td>
<td></td>
<td>0.04 mol/kg</td>
</tr>
</tbody>
</table>

4.2 “Rising damp” and salt fractionating

Everybody is familiar with the concept of “rising damp” although it can be considered a misnomer, as “damp” is defined as diffused moisture in air, that is, water vapor, while the actual process corresponds to liquid water transport in a porous material [55, 56].

To illustrate the point, the example of a building suffering from rising ground moisture over many centuries can be used. Rising damp results from the capillary absorption of ground water by the porous network of the material. Ground water, mainly originating from rain, or other surface water sources such as broken pipes, seeps through the soil dissolving part of the salts that may be present, such as nitrates, chlorides, and sulfates. The height that capillary rise can reach in a building will depend both on the pore structure of its materials as well as the thermohygric conditions found at the surface of the material, but as a rule of thumb this height will oscillate around 15 cm [57]. This is an average value and the authors estimate that it could reach some 25 cm or even up to 100 cm under some conditions [56]. If, however moisture is found above this value, it is practically a certainty that salts are present in it [58–60]. Figure 5(left) and (right), illustrate this point, which is poorly understood and has led to some confusion. In general practice, dampness found at 2–3m height is still attributed to “rising damp” [61] when this problem may be related to infiltrations from the roof, malfunctioning gutters or leaking interior pipes, and/or a combination of ion transport and hygroscopicity as discussed subsequently.

Seldom will only one salt be present in a building; usually two or more salts will be dissolved in the water that enters a structure. As the water rises by capillarity, evaporation will also take place, so that the less soluble salts will precipitate out first, closer to the entering point of the water, i.e., near the ground, while the more soluble...
ones will rise higher in the wall [29, 62, 63]. To illustrate this point, the following situation is considered: a house with “rising damp” problems where the water during its percolation through soil acquired the most common ions generally found, i.e., the cations sodium (Na\(^+\)), potassium (K\(^+\)), magnesium (Mg\(^{2+}\)) and calcium (Ca\(^{2+}\)); and the anions chloride (Cl\(^-\)), sulfate (SO\(_4\)\(^{2-}\)), nitrate (NO\(_3\)\(^-\)) and bicarbonate, (HCO\(_3\)\(^-\)). The most insoluble salts will form close to the ground, such as calcite (CaCO\(_3\)) calcium carbonate, and gypsum (CaSO\(_4\).2H\(_2\)O) calcium sulfate dihydrate. These can appear as whitish films or crusts. As the solution, now enriched in the other ions, continues to migrate upward and with on-going evaporation other salts will crystallize out, such as the magnesium sulfate, either as epsomite, (MgSO\(_4\).7H\(_2\)O) or as hexahydrate (MgSO\(_4\).6H\(_2\)O) depending on the thermo-hygic conditions. Similarly, sodium sulfate can crystallize as the decahydrate mirabilite (Na\(_2\)SO\(_4\).10H\(_2\)O) or the anhydrous thenardite (Na\(_2\)SO\(_4\)), if the temperature at the time of crystallization is above 32.4°C or at a low RH. During cold periods of the year, potassium nitrate crystallizes out as niter (KNO\(_3\)) as the solubility of this salt is highly temperature dependent. These salts tend to form the most visible efflorescence found in the region above that of the more insoluble salts. Fractioning of the salts within a wall has been observed and studied for many years [62, 64] and obviously depends on the ions present in the water [28–30].

Chlorides and nitrates are the most soluble salts and will therefore be last in crystallizing out, such as the alkali salts: halite, NaCl sodium chloride, niter, KNO\(_3\) potassium nitrate, or nitratine, NaNO\(_3\) sodium nitrate. More soluble and hygroscopic chlorides and nitrates of alkaline earth metals, such as calcium chloride used as a deicing salt, will hardly ever crystallize out but will keep these areas damp at all times.

Finally, it is important to recall that the less soluble salts, such as gypsum and calcite, will have a significantly increased solubility in the presence of salts such as NaCl or KCl, i.e., salts that do not have a common ion with them (see Table 1). Therefore, these salts that in principle are found to crystallize mostly at the lower parts of the building, may also be found efflorescing at several meters high [45, 46]. Furthermore, it is to be considered, that efflorescence can re-enter the pore structure when wetted by rain or when cleaned with water, e.g., during a conservation intervention, resulting in a redistribution of salts and their concentrations at different depths and heights of the wall in question.

4.3 Efflorescences and subflorescences

Efflorescences will form when salt bearing water evaporates straight from the surface of the material and salt crystallization takes place on the surface. These do minor damage to the porous material as they just grow on the surface and can easily be brushed off. However, if there is paint on the surface, such as in the case of mural paintings, this will be damaged by the growing crystals as they...
will push it away and the paint will tend to powder or flake off, depending on the nature of the paint (Figure 6).

When the flow of water is slower than the evaporation rate of the water, the evaporation front will move inwards from the surface and subflorescence will form. As these crystallize within the pores of the material they cause damage (see Figure 1). The location where salts will concentrate is a balance of two mechanisms: 1. flow of the salt solution towards the evaporation surface; and 2. the return migration of the concentrating ions at the evaporation surface into the solution as a result of concentration differences. The first mechanism is sometimes referred to as advection [65–67] or convection-diffusion [68], while the second is a diffusion process [65]. A simple mathematical model describing this mechanism can be found elsewhere [68].

The crystal habit acquired by salts in efflorescence provides information of the conditions under which the crystallization took place. This has been studied in detail by Arnold and Zehnder [63, 64, 69]. If the crystallization takes place when the surface is wet and a good supply of water is available, relatively large crystals will develop in the most common habit of the salt, i.e., cubic for halite, rhombohedral for nitratine, etc. As less water becomes available, smaller crystals will form with rounded edges. With decreasing water availability, fibrous crusts will form, with columnar crystals growing perpendicular to the surface and away from it. This is finally followed by the formation of whiskers, i.e., very thin crystals (see Figure 7).

While in general, different salts crystallize forming independent crystals, there have been many instances found in which different salts actually intergrew, indicating a change in ionic supply during the time of crystal growth [70]. Figure 8 illustrates the case of an intergrowth of whiskers formed alternately by halite and by nitratine.
4.4 Porosity and its effect on liquid transport

Over time, salts will accumulate within the porous material so that when water enters the masonry, either by infiltrations, rain or condensation, it will dissolve them allowing their migration within the material in various directions. The crystallized salts will tend to accumulate where water evaporates. How water will move through the masonry will be influenced by the porous structure of the various materials making it up, e.g., stone, brick, mortar, render and their combination [35, 60, 71–74]. The location of the evaporation front, i.e., the place where water evaporates, is dependent on both the thermohygric conditions, i.e., RH and temperature, under which the evaporation takes place; and, the porosity of the material, i.e., pore size distribution, connectivity, etc. [35, 75].

The shape and environment of the building will play an important role. For example, corners will evaporate faster than a flat surface because of a higher specific surface and because air circulation will be enhanced by protruding features. That is why fluted columns generally show deterioration at the flute edges. Considering equal thermohygric conditions, evaporation will occur preferentially in materials with higher porosity and well connected coarse pores [76, 77]. This also explains why lime mortars in historic structures weather away first, as they have a higher porosity and lower mechanical strength than the brick or stone they bind so that salts will concentrate there. When these buildings were repointed using a more resistant and less porous material, such as Portland cement mortar, then the brick or the stone would deteriorate (Figure 9) leading to a damage that cannot be repaired as easily.

For materials with a heterogeneous bimodal porous system, i.e., a combination of large and small pores, damage will occur in the latter ones because that is where the water will be retained longest [56]. When only a relatively low salt burden is present, saturation will mostly occur when water has retreated into these small pores and therefore crystallization will take place within them. Examples of this can be found in natural stones that contain pockets of laminar minerals, such as clays or micas, or schistose materials. These will weather out faster than the surrounding matrix because water will concentrate in them [78–81] as shown in Figure 10. While swelling of clay minerals may play a role, the combination of clays and salts increases the deterioration rate as discussed in more detail subsequently [72].

Figure 9: Old brick masonry wall in a garden that was repointed with a cement mortar. Note that major damage occurs in the center area where salts crystallize out as subflorescence (between half a meter to 1 m height) and that the bricks are damaged first being more porous than the cement mortar. The lower area, where the wall is mostly damp, concretions tend to form with salt efflorescence right above it, but less damage is evident.

Figure 10: Molasse sandstone in the Fribourg city wall. The Burdigalien formation often contains inclusions of very fine-grained marl (a calcareous mudstone) with fine pores that tend to weather out first.
Drying, similarly to water absorption, is determined by the pore sizes. The larger pores will lose water first [82, 83] but the presence of salts, because of their attraction for water will decrease the drying rate. To be remembered is that salt solutions will boil at a higher temperature than pure water; or, the equilibrium RH for water is 100% but this will be lower for a salt solution. Furthermore, there are changes in the wetting properties for materials when salts are present, e.g., increase of the contact angle between liquid-air and solid-liquid interface [84].

The drying rate may also be decreased by salt crystals blocking pores near the drying surface [58]. In particular, the crystallization of gypsum has been shown to have a significant effect in delaying moisture evaporation [85] and in the transfer of dilation stresses [72, 86]. The amount of damage caused by salt crystallization is also influenced by the porosity and pore size distribution of the materials, as different salts may tend to crystallize in different locations [73]. However, when efflorescence is present, the total evaporation area increases and the drying rate might be increased [65, 67].

4.5 Salt hygroscopicity and its consequences

Hygroscopicity is the sorption, or adsorption, of water vapor, henceforth called moisture, from the environment. All materials undergo this process to a major or minor degree. Wood, for example, is particularly prone to this phenomenon and when the air is moist – high RH – it expands because of the sorbed moisture. Inorganic materials also adsorb moisture, but to a far lower degree. As moisture sorption occurs at the surface, it follows that materials with a high specific surface, i.e., surface per unit weight, will absorb more moisture. Therefore, the presence of clays, with their usual platy structure, small grain size and hence big internal surface, increases this process significantly [87]. Swelling clays have been studied for years, e.g., Madsen and Müller-von Moos [88], and continue to be studied within the stone deterioration context [72, 89–92]. It is important to remember that the type of porosity is critical. Materials with similar overall porosity may absorb differently because of the different type of porous network [87].

Salts, as any material, will also be hygroscopic [93, 94]. But their hygroscopicity is compounded by the fact that a salt solution has a lower vapor pressure than that of pure water at the same temperature. Since relative humidity, RH, is the ratio of the water vapor pressure present in the air at a given temperature to that of the saturated water vapor pressure at the same temperature, it follows that one can define the equilibrium relative humidity, RHeq also referred to as deliquescent relative humidity DRH, of a saturated salt solution, as the ratio of the water pressure over the saturated salt solution to that of the saturated water vapor pressure at the same temperature.

For example, sodium chloride, one of the most ubiquitous salts present, has a 75% DRH. This means that if this salt is present in a porous material and the RH in the environment rises above 75%, the salt will rapidly sorb moisture and tend to go into solution, a process called deliquesence. Therefore, if the above material is examined on days where the RH is below 75%, the material will appear dry, but if the RH is above this value, it will appear moist, hence the recommendation that buildings be inspected on both dry and damp days.

In the case of salt mixtures, the solution does not have a single DRH but rather a range of relative humidity above which it will be deliquescent. For example, at 25°C a saturated sodium sulfate solution has a 91.4% DRH, while that of a saturated sodium chloride solution is 75.3% [95:109]. However, if these salts are together in solution, the system will deliquesce between 74.5% and 80.5%, because the composition of the system will vary during this process. As has been summarily expressed by Steiger and Dannecker [96], at 74.5% RH the NaCl will deliquesce at the expense of the hydration water of mirabilite, the stable solid phase at that temperature (Figure 11).

When the salt, or salt mixture, is found within a porous material the total amount of moisture sorbed will be a function of both the pore structure of the material and the nature and amount of salt present [59, 97–100]. A simple experiment can be carried out by subjecting the finely powdered table salt (NaCl) to a RH > 90% and it will be seen that the powder heaves as it absorbs moisture (note that commercial table salt may contain anti-caking agents or other ingredients that will alter its behavior). Although initially the salt will expand, as deliquescence sets in, it will shrink as it goes into solution because its ions attract water molecules that will form hydration layers around them and, because of the attraction, occupy less volume than water by itself.

A similar behavior is shown by other porous inorganic materials, in particular those containing expansive clays. In this case, the expansion is mainly due to the presence of the clays, and in general, the cycle can be repeated many times before deterioration sets in. If however, salts are present, the behavior is completely different. At RH above the DRH of the salt present, there is an initial contraction (water is being bound by the salt) and, when the RH falls
below the DRH there is an expansion to approximately the original size. But in these cases, the cycle is not quite reversible so that there is an overall increase in the expansion observed because of the salt crystallization, and it does not revert to the initial “size” [72, 88, 103].

This behavior was also studied using a lime:cement:sand (1:4:20) mortar in which some samples were contaminated with NaCl [101]. Both control and salt contaminated samples (approximately 2% w/w) were cycled between 10% and 90% RH at 20°C. The control samples expanded slightly upon being exposed to high humidity (as expected for an inorganic porous material) and shrank somewhat when exposed to low humidity, and this was repeated for the six cycles the experiment ran (Figure 12). On the other hand, the salt containing sample contracted upon being exposed to high humidity for the first time and then expanded when the salts crystallized out. However, with each cycle, the amplitude between the expansion and contraction increased and the overall expansion of the sample increased with the number of cycles becoming irreversible.

The mentioned study by Lubelli [101], also showed that other salts, i.e., NaNO₃ and KCl, behaved similarly, though there were slight time differences for the expansion to start, reflecting the different kinetics between salts. All salts tended to coat the pore surfaces fairly uniformly, confirming previous studies carried out with NaCl [103], NaNO₃ or NaCl [104]. This salt layer, formed by small crystals (< 20 µm), is very hygroscopic because of its high specific surface and is known to have a tendency to creep [105].

Salt creep studies date back to the early twentieth century [106–108]. The relevant salts for building deterioration that show this behavior are NaCl, KCl, NaNO₃ and KNO₃ as they form thin salt films. The mechanism is attributed to the fact that crystallization will begin at the meniscus formed by the solution in contact with the pore wall, where the crystallizing salt tends to form a crust on the solution surface, leaving a narrow space that acts as a capillary between the crust and the pore wall so that the solution will move up and repeat the process [109, 110]. What is also interesting is that this mechanism, especially for sodium and potassium chloride, occurs with what was described as “flooding” events. During these events, the advancing crystals would suddenly be inundated by a relatively large quantity of solution [110].
These events are similar to those observed during the dehydration of thenardite as described elsewhere [98]. Pühringer [111] had suggested that salt creep contributed to the migration of salt within a porous material and graphically described this by stating “that salts take up moisture and transport it” [105].

To clarify the mechanism, Figure 13 shows the DRH changes for the four mentioned salts, chloride and nitrate of sodium and potassium, as a function of temperature. Included in the graph are the corresponding changes of RH with temperature for two absolute humidity levels, 14 and 16 g/cm³. It can be seen that a 5°C temperature change, from 25°C to 20°C, will make the two sodium salts (at 14 g/cm³) and a third one, KCl (at 16 g/cm³) deliquesce and subsequently creep upon crystallization.

It has been postulated that salt adherence to pore surface may induce stresses to the pore surface upon salt expansion [99, 110, 114]. However, other researchers consider this unlikely as salts will always have a solution film between them and the pore wall [51, 115] plus the fact that when crystallization modifiers were added to the crystallizing salt no expansion of the sample was measured when subjected to RH above 75%. Electron microscopy examination of the samples showed that when the crystallization modifiers were added the salts no longer formed layers coating the pore walls but formed isolated agglomerates that crystallized in a different habit as expected [101].

Temperature changes will also result in expansion of the porous material and of any salt present in it. If the salt is hydrated its dehydration will proceed by cycles of contraction-expansion (caused by recrystallization) until all salt is totally dehydrated [116]. Finally, a common belief is that if a salt laden object is kept at a relative humidity below its DRH, such as a salt-contaminated ceramic in a museum, no damage can occur [53]. However, this is not the case as demonstrated in a study where salt containing ceramic tiles were subjected to RH cycling below the DRH of the salts in question [117] (Figure 14). The tiles shown in the figure were immersed in NaCl + CaSO₄·2H₂O solution for at least 23 h. This solution was prepared by mixing equal amounts of saturated solutions of NaCl and gypsum, adding extra NaCl.
and gypsum to the mixture and letting the solution equilibrate for a week. As long as there are RH fluctuations, salts will induce deterioration by expansion-contraction cycles. If these cycles cross the DRH (for the case of a single salt) or the DRH range (for a mixture), more deterioration will occur because there also will be solubilization-recrystallization cycles. Similar results have been observed on actual buildings when monitoring interiors as for example in the Suomenlinna fortress in Finland [10].

5 Discussion

“Rising damp” is often blamed for most of the problems related to salt damage and it has been shown that this is not the case. Once salts are within the porous material, their hygroscopcity, especially above the equilibrium RH or RH range, will lead to their deliquescence, creep and partial recrystallization so that their mobility is increased significantly. Daily changes in temperature will induce corresponding RH changes, so that within one day, there may be many cycles during which the salts will deliquesce, creep and recrystallize. This explains how salts tend to accumulate in walls at heights above two meters. One of the key points to be taken into account is that seldom do these crystallizations occur under equilibrium conditions.

The damage induced can be explained as follows: the salt distribution in the porous material is not necessarily uniform, since porous materials are rarely uniform and this influences moisture distribution in them [103, 118]. Therefore some areas within the material may have a low salt concentration while others have a high one. Upon changes of RH, there will be expansion and contraction of the material. If the RH cycling is below the equilibrium RH or range, then the material will expand more than the salt contaminated sample [101–2] but these expansions and contractions are reversible. However, if the RH cycling crosses the equilibrium value of range for the salts presents, then while the material expands upon moisture absorption, the salt contaminated one contracts and upon further cycling these dimensional changes turn irreversible. Since a porous material in a building exposed outdoors can seldom be considered at equilibrium – its surface temperature will be different from that in its interior and the salt concentration at the surface/subsurface will be dissimilar to that in the interior – stresses acting in opposite direction may develop. Even if these stresses are minimal, the repeated long time cycling will frequently induce material fatigue. Complementing this damage is the mechanical disruption caused by the crystallization of the salts transported by the convective flow of moisture to the surface of the material where they will form efflorescence/subflorescence.

It is extremely difficult to compare data obtained from different salts or salt mixtures studied on materials with different pore systems and mineralogical composition. What is most important is how water will move out of the pore system at the time a wet material is drying. As has long been known, water will be retained longer in the fine pores [119] and understanding water movement through the capillary system for the specific material in question is fundamental for determining where salts will crystallize out [82].

While the physical processes that lead to salt deterioration are not completely understood as yet, much experience has been gained from laboratory studies and examination of actual buildings including in situ testing for over a century. The following points summarize the most relevant general issues that need to be considered:

- Salts present in porous building materials originate from different sources and enter the pore system in solution, and therefore are very mobile.
- When the water in the salt solution evaporates, salts crystallized out within the pore system exert mechanical pressure on the material inducing damage.
- Each salt turns hygroscopic above the DRH, while for a salt mixture, this will be a DRH range.
- All porous materials absorb moisture at high RH. If they contain soluble salts they will absorb significantly more.
- Salt efflorescence on the material surface may appear not to cause much damage but it serves to indicate that salt(s) is present in it.
- For a given material under identical climatic conditions, more salt means more damage.
- Large and/or fast fluctuations in RH and T will result in more damage to the material than minor and/or slow fluctuations.
- Materials with very heterogeneous pore systems, i.e., both fine and coarse pores, will generally suffer more damage from salts than those with homogeneous pore systems.
- For materials with a relatively homogenous pore system, those with fine pores will suffer more damage than those with coarse pores.
- The more complex the mixture of salts present within a material, the more damage is to be expected.
6 Conclusions

Once the presence of salts has been established, the following two points should help in finding an appropriate solution:

1. Determining if there is an active water ingress to the building/structure (rising damp, leaking roofs, gutters and drains);
2. Identifying which are the most important salts present and whether they accumulated over years, or are still actively being introduced into it.

There are many solutions to this complex problem and this topic deserves a review of its own. However, solutions may be classified into the following four broad categories (some key references are provided), which may have to be combined depending on the problem faced:

- Reduction of water infiltrations in general, including damp-proof barriers [57, 120, 121].
- Desalinization via poultices [122–124].
- Special salt retaining renders or sacrificial renders [125–127].
- Immobilization of gypsum via the Florentine method [128–130] based on solubilization of gypsum with ammonium carbonate, immobilization of the sulfate with barium hydroxide and, if necessary consolidation of ammonium oxalate.

As with any conservation intervention, there is no single solution that is applicable to all cases. Each case is unique and requires a specific approach developed for it. Only then can we hope to achieve a good working solution.

Acknowledgements: The authors would like to thank Prof. Josef Pühringer for encouraging us to develop this topic into a summarizing paper. Also to be acknowledged for their comments and suggestions are Dr. José Delgado Rodrigues, Dr. Bénédicte Rousset, and Arq. Marcelo L. Magadán.

References

22. Fitzner B. Documentation and evaluation of stone damage on monuments. In: Kwiatkowski D, Löfvendahl R, editors. 10th Int


100. Lombardo T, Doehne E, Simon S. The response of NaCl and Benavente D, Cueto N, Martínez-Martínez J, García del Cura A. E. Charola and C. Bläuer: Salts in Masonry


