



# **‘Paula’s Papers’: Salts in Porous Construction and Building Materials**

## **Paper 1 – Types and Sources of Salts**

**February 2020**

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## 1. SALTS IN POROUS MATERIALS: WHAT ARE THESE AND WHY ARE SALTS SO BAD?

Soluble salts are one of the most important and frequent weathering agents causing decay of porous building materials. Salts originate from ions that have been leached out from different sources and are carried in diluted aqueous solutions. They may penetrate the porous materials and circulate through their cavities and pores. The main mechanisms responsible for the introduction of soluble salts into the porous materials of a building are capillary movement of groundwater and infiltration by rainwater. The dissolution, mobilisation and further salt crystallisation will depend on the amount and interaction of water/vapour ingress through porous materials, the number, size and connectivity of porosity, the type and concentration of salts either in the water or materials, and the surrounding environmental conditions.

Salts concentrate and accumulate where the solution evaporates. Some of the main salts present on walls are carbonates, sulphates, chlorides, nitrates and oxalates of sodium, potassium, calcium, magnesium and ammonia. The growth of salt crystals within the pores can generate forces high enough to break down building materials into fissures, flakes, scales or even disaggregate them into powder (*Fig. 1*).



**Fig. 1:** Rock-cut façade (Silk Tomb) at the Archaeological Park of Petra (Jordan). Decay of Nubian sandstone (quartzarenite) affected by salt crystallisation of niter ( $\text{KNO}_3$ ) related to human and animal activity. More secluded monuments are affected by gypsum from the geological origin of the rock.

Salts may also absorb moisture from the atmosphere, change their hydration state, dissolve, crystallise and eventually causing damage by repeated crystallisation cycles due to environmental fluctuations. More on this later.

## 2. WHERE ARE THESE SALTS COMING FROM?

To determine the source of the salts is important for finding the right solutions to avoid decay of building materials. The type of salt can also help us determine the source (although, most often, there is not just one single source but a combination of them). The final composition, distribution and behaviour of these salts will depend on the physico-chemical reactions between materials and solutions. Building materials can be affected by many sources, such as soil/groundwater with salts rising by capillarity; salts from air polluted rain or blown by the wind from the sea or the desert; from unsuitable cleaning products, incompatible building materials, and others.

### 2.1. Salts from soils and ground waters

Ground waters are diluted salt solutions with higher or lower concentration depending on the geology and soils of the regions through/along which these waters pass. These salt solutions are composed by a combination of ions, i.e. cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc.) and anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , etc.).

During rising damp, the mobilisation and mixture with the composition of the building materials can happen as well. The efflorescent marks that are sometimes observed at the evaporation front of the rising damp can be a combination of one or both sources. Compared to normal soil solutions, those near human latrines and/or animal living areas or farms are often enriched in ammonium/nitrates and chlorides due to contamination by urine and other excreta and subsequent microbial activity.

### 2.2. Salts from marine aerosol and air pollution

Atmospheric aerosol or marine spray is also a source of chlorides. Sea salt particles have a chemical composition very similar to that of bulk sea water ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  which major ions are  $\text{Na}^+$  and  $\text{Cl}^-$  (85.6% of the bulk sea salt). Building materials exposed to polluted atmospheres are severely affected by past or current acid deposition. Atmospheric acidity give rise to sulphur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ) that may give rise to formation of sulphates and nitrates.

The effect of coal burning, release of  $\text{SO}_2$  gases from decomposition of impurities (e.g. pyrites (sulphides)), generation of acid rain (sulphuric acid) and reaction with limestone (calcium carbonate) form gypsum (calcium sulphate) black crusts mixed with soot and organic matter. This was a sign of past environmental air pollution that is currently reduced and washed away by the action of rain. However, the salts remain at the surface and still may deteriorate the building materials due to environmental fluctuations (Fig. 2).



**Fig. 2:** Howden Minster Cathedral (near Goole, Yorkshire, UK). Gypsum black crust and presence of other salts.

### **2.3. Salts from building materials and related products**

Salts also can be part of the original composition of the building materials, either from their own geological origin or generated during the manufacturing process. Lime mortars in old buildings are very often made from burning limestone containing dolostone (i.e. magnesium limestone) and impurities such as pyrites. The weathering process involve physical and chemical reactions that give rise to magnesium sulphate salts.

Cleaning acid and alkaline products, treatments with 'waterglass' consolidants, injections of Portland cement, alkali silicates, siliconates and similar products may also form soluble salts. Their use is not always detrimental but possible secondary effects always have to be considered, since they may become harmful when used inappropriately in the wrong place, or in ancient buildings and monuments.

Ettringite and thaumasite are complex sulphate salts that decay materials reinforced with concrete and Portland cement. Hardened Portland cement may contain soluble alkalis (based on  $K^+$  or  $Na^+$ , e.g.  $Na_2O$ ) that may form alkali carbonate salts (e.g. natrite ( $Na_2CO_3 \cdot 10H_2O$ )). The reaction with sulphuric acid from polluted air may form mirabilite ( $Na_2SO_4 \cdot 10H_2O$ ). Whereas water glass (i.e. solution of sodium or potassium silicate which solidifies on exposure to air) is the binding medium of the silicate paints – it was frequently used in the past for the consolidation of stone monuments, lime mortars, plasters and wall paintings. This formed a hard surface layer leading to accelerated spalling.

### **2.4. Other sources of salts**

Deicing salts (e.g.  $NaCl$ ,  $CaCl_2$ ,  $MgCl_2$ ), soil fertilizers (e.g. phosphates, nitrates, sulphates, chlorides of  $K^+$ ,  $Ca^{2+}$ , etc.), storage of salts for meat preservation (e.g.  $NaCl$ ) or even for gunpowder ( $KNO_3$ ) in historic buildings, are other salts sources. It has also been reported that salts are commonly found by building surveyors in or close to fireplaces of many residential buildings. However, there are no scientific publications available on the composition of these salts and how to deal with them in a cost effective, non-detrimental way.

Salt ions leached out of the ground, from the building materials, the polluted atmospheres and from biological metabolism, circulate in aqueous solutions within the walls and porous materials. Where water evaporates, the soluble salts concentrate and different phases precipitate where and when supersaturation is reached.

## **3. HOW DO THE SALTS INTERACT WITH THE ENVIRONMENTS?**

The processes of leaching out, transport, evaporation, accumulation, solute concentration and crystallisation occur by the action of water movement and drying out. Once water (liquid) and/or moisture (water vapour) enters the porous materials, damage takes place when salts solutions move and crystallise within the pore structures. Water as liquid will transport salts by capillarity being able to dissolve other salts present in the materials. Water as vapour (e.g. a humid environment) moves by gaseous diffusion and it may be retained by materials through hygroscopicity.

### **3.1. Hygroscopic and deliquescent salts**

Hygroscopicity is the ability of materials to attract moisture from the air. The material itself can sorb- (i.e. ad- and/or ab-sorb) a certain degree of moisture depending on its nature. All soluble salt crystals may deliquesce (i.e., take water vapor from the surrounding atmosphere and dissolve in it (becoming liquid) forming a saturated solution. The relative humidity (RH) of the air determines whether a salt crystallises or dissolves.

Hygroscopic salts are highly soluble salts that trap vapour from the environment and dissolve (deliquesce) *at lower RH conditions*. The deliquescence RH or equilibrium RH (RHeq) is the critical value of RH between the crystallisation and dissolution process. The higher the hygroscopicity of the salt the lower its RHeq. *Supersaturation* is a condition for salt precipitation (i.e. crystallisation). Evaporation will cause the saturation of the salt solution depending on the chemical composition, temperature (T) and RH.

A saturated salt solution will crystallise if the RH of the surrounding environment is lower than the RHeq of the concerned salt. Whereas if the ambient RH is higher than RHeq, the salt will remain in solution. Each salt phase has its corresponding RHeq for a given temperature: *Table 1* shows the solubilities and RHeq of some common salts.

	Salt Solubility in grams per 100 cc		RHeq (%) at 20°C
	Cold water	Hot water	
Sodium chloride (halite: NaCl)	35.9 <sup>20</sup>	39.4 <sup>100</sup>	75.5
Sodium sulphate (mirabilite: Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O)	11 <sup>0</sup>	92.7 <sup>30</sup>	93.6
Sodium sulphate (thenardite: Na <sub>2</sub> SO <sub>4</sub> )	4.76 <sup>0</sup>	42.7 <sup>100</sup>	87
Magnesium chloride (bischofite: MgCl <sub>2</sub> ·6H <sub>2</sub> O)	54.25 <sup>20</sup>	72.7 <sup>100</sup>	33.1
Magnesium sulphate (epsomite: MgSO <sub>4</sub> ·7H <sub>2</sub> O)	71 <sup>20</sup>	91 <sup>40</sup>	90.1
Calcium chloride (antarcticite: CaCl <sub>2</sub> ·6H <sub>2</sub> O)	74.5 <sup>20</sup>	159 <sup>100</sup>	30.8
Calcium sulphate (gypsum: CaSO <sub>4</sub> ·2H <sub>2</sub> O)	0.24 <sup>0</sup>	0.22 <sup>100</sup>	99.9
Potassium carbonate (potash: K <sub>2</sub> CO <sub>3</sub> )	111 <sup>20</sup>	156 <sup>100</sup>	43.2
Potassium chloride (sylvite: KCl)	34.4 <sup>20</sup>	56 <sup>100</sup>	85.1
Potassium nitrate (niter: KNO <sub>3</sub> )	31.6 <sup>20</sup>	243.6 <sup>100</sup>	94.6

**Table. 1:** Solubility and deliquescence humidity (RHeq) of some frequent salts in buildings

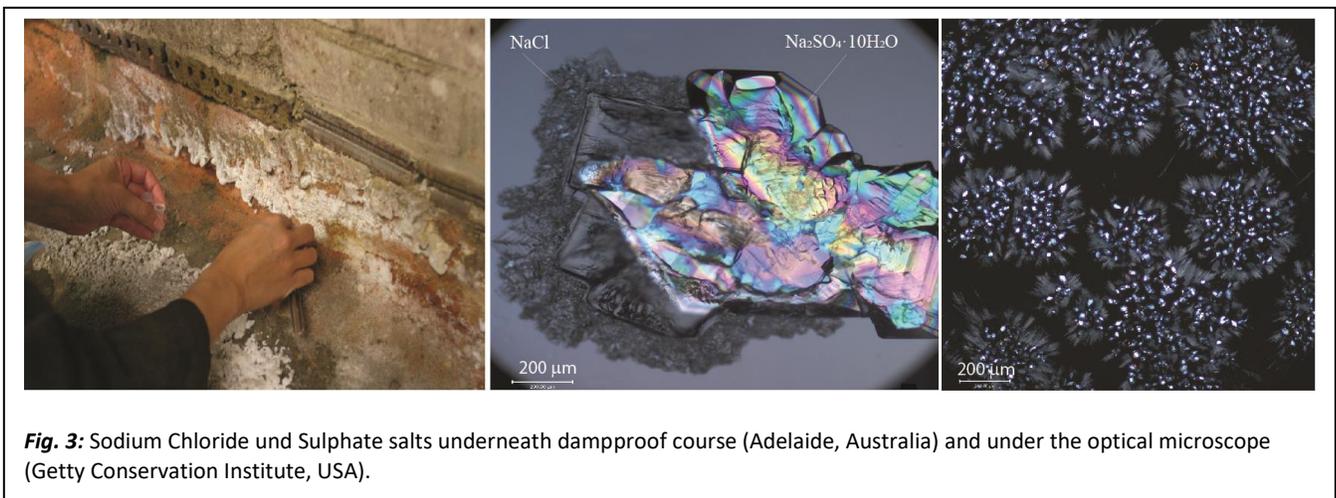
For example, with sodium chloride (NaCl, rock salt, table or common salt), frequently used as deicing salt, RHeq has almost no T dependence and will be dissolved above 75% RH and crystallise below. Highly hygroscopic salts that do not crystallise under humid environments are often present in undamaged zones. Sodium and potassium salts and all sulphates show deliquescence humidity's (RHeq) greater than 70% RH. The deliquescence of alkali earth (eg. Mg<sup>2+</sup>, Ca<sup>2+</sup>) chlorides and nitrates occur at considerably lower RH (<60%).

In contrast, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O, hydrated calcium sulphate) with a RHeq > 99.9%, which has a very low solubility, is essentially non-hygroscopic. The reaction between alkaline building materials (e.g. cement, lime, etc.) and Waterglass products may produce potassium carbonate which has a low RHeq (cannot easily crystallise) and may just form non-aesthetic hygroscopic damp stains. However, may also form potassium sulphate, chloride or nitrate, which are less hygroscopic and therefore crystallise at higher RH, becoming more destructive.

### 3.2 Hydrate-forming salts

Some salts are hydrate-forming salts which can also change their hydration state as a function of Temperature and RH. The phase change from the lower hydrated (or anhydrous) form to the higher state of hydration causes an increase in volume. This hydration expansion is considered an important cause of salt crystallisation damage as the result of crystal growth from supersaturated solutions, if the hydration reaction proceeds via dissolution-crystallisation mechanism. Crystallisation pressures are higher than hydration pressures within the pores.

The best example of hydrate-forming salt is sodium sulphate, frequently affecting concrete structures and considered one of the most damaging soluble salts. It can exist as the anhydrous salt (thenardite,  $\text{Na}_2\text{SO}_4$ ) or containing ten molecules of water (i.e. decahydrate, mirabilite,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). The former increases in volume by more than three times with increasing humidity during the transformation to the latter. This occurs through a hydration-dissolution-recrystallisation mechanism producing very high crystallisation pressures and hence a greater destruction of porous building materials (*Fig.3*).



### 3.3 Salt mixtures

The reality is that salt systems are more complicated mixtures of ions. The values for the RHeq of pure salts may not apply directly, being only indicative. Capillary rise and evaporation of ground water usually leads to an accumulation of a very hygroscopic salt mixture. There is a dynamic equilibrium between the masonry moisture content and the ambient RH. Moisture is picked up as RH increases and water evaporates from masonry as RH decreases. Upon evaporation the solution becomes increasingly concentrated, and eventually supersaturated regarding one or more salts that will crystallise. If masonry was contaminated with a single salt that would be simple and it would crystallise if the ambient RH drops below its deliquescence humidity (RHeq). However, the behaviour of salt mixtures is more complex.

Crystallisation in mixed salt systems occurs across a range of RH rather than at specific values. Considering the range of T and RH in the built environment, common salt mixtures in porous materials are subject to continuous phase changes that can be more, or less damaging to construction and porous building materials.

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