

A review of salt transport in porous media : assessment methods and salt reduction treatments

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A review of salt transport in porous media, assessment methods and salt reduction treatments

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Abstract

It is an unpalatable fact that while objects can deteriorate through lack of care and attention, they can also deteriorate as a result of inappropriate and misguided interventions. This is particularly the case with regard to salt-related deterioration problems. A successful treatment outcome using aqueous salt reduction methods demands an understanding of the transport processes involved as well as detailed information regarding the characteristics and specific situation of the individual object.

The use of poultice materials to reduce the salt content of salt deteriorated objects is a long established technique in conservation. However, due to the complex nature of salt problems within historic structures the result of such interventions can be variable and unpredictable. The amount and depth to which salts are mobilised, and where they are transported to, is dependent on the inter-relationship between the poultice and the substrate, the drying conditions and also the initial salt distribution.

This paper examines the current scientific understanding of salt and moisture transport processes, and the extent to which this knowledge can feed back into the practical arena, to aid the conservator. Moreover, areas where further research is required are identified. In particular, the importance of pre- and post treatment investigations is highlighted, showing how, in combination with knowledge of salt and moisture transport mechanisms, these can give useful indications regarding treatment options. The role of selective salt extraction and the post treatment behaviour of residual salts are discussed.

Keywords

salt extraction, poulticing, cultural property

1. Introduction

Objects affected by salt deterioration require multi-disciplinary expertise to inform a conservation strategy [WTA Merkblatt 2003]. Nonetheless, it is the conservator, not the architect or the scientist that faces the practical task of treating an object. This is a tremendous responsibility, made all the more challenging by the fact that our current scientific understanding of deterioration processes in general is incomplete—notably so with respect to salt deterioration. Indeed, while scientists are still currently wrestling with fundamental issues such as the mechanisms by which crystallisation pressure develops in porous media [Flatt *et al.* 2007], conservators equally face significant challenges of their own in relation to treatment selection and application.

This paper examines the current scientific understanding of salt and moisture transport processes, and the extent to which this knowledge can feedback into the practical arena, to aid the conservator. Accordingly, the following has been structured in two parts. Section I summarises the current state of knowledge regarding salt and moisture transport in porous media, while Section II outlines and discusses practical issues, such as assessment methods and salt reduction treatments. Particular attention is paid to the extent to which our current understanding of salt and moisture transport can answer practical questions of relevance to the conservator, and where significant gaps in that knowledge lie.

2. Salt & moisture transport. How does it work?

The damage caused by soluble salts is generally due to their accumulation and phase transitions at or near the surface of the object, or between layers, as a result of moisture transfer processes. Consequently, moisture can be regarded as the main catalyst for salt damage—indeed, without moisture transport processes there would be no salt damage. The severity of damage caused is related to the location of salt crystallisation: on a microscopic scale the distribution of crystallisation sites with respect to pore size has been identified as an influential factor in damage [Flatt *et al.* 2007, Scherer 2000, Rodriguez-Navarro and Doehne 1999, Wellman and Wilson 1965, Rossi-Manaresi and Tucci 1991, Fitzner *et al.* 1996]. However, on a more macroscopic scale the salt and moisture transport processes determining whether crystallisation occurs within the porous matrix (subflorescence) or at the surface (efflorescence) are also highly important. Although visually alarming, efflorescences are generally less harmful than subflorescences, which cause the disruption and loss of the object's surface, the consequences of which can be extreme—particularly so in the case of wall paintings. Therefore, the study of salt and moisture transport in porous media is necessary to:

- understand the evolution of damage mechanisms;
 - correctly evaluate damage phenomena;
 - develop and select interventions, and assess their outcome;
-

- give a reliable prognosis of future damage.

The location of crystallisation results from the dynamic balance between three rate processes, which determine the ultimate solute distribution:

- i. the rate of moisture loss through evaporation;
- ii. the rate of moisture supply by capillary flow;
- iii. the rate of ion back diffusion due to the concentration gradient established within the salt solution.

Relatively simple models to describe how the balance between capillary transport and evaporation processes determine the zone of salt accumulation and crystallisation are available [Lewin 1982, l'Anson and Hoff 1986, Garrecht 1992, Hall and Hoff 2007]. However, more complex arguments come into play when one also considers the roles of salt transport by advection (capillary flow) vs. diffusion (according to a concentration gradient), the effect of solution properties (such as viscosity), and also the porous support structure. The following is, therefore, a summary of the current state of understanding of these issues in relation to the salt deterioration of porous objects.

2.1 Moisture and ion transport

In figure 1 a schematic representation is given to show the drying process of a porous material saturated with a salt solution. During drying, liquid moisture is transported to the surface where it leaves the material by evaporation. In general, the drying of a homogeneous, uniformly wet, porous material has two identifiable stages: first a uniform drying period, followed by a receding drying front period. During the first period, moisture transport is fast and takes place in the liquid phase. Drying then proceeds by evaporation from the material surface. Consequently, the rate of moisture loss from the material is constant as long as the rate of capillary supply to the surface is greater than or equal to evaporation. The evaporation flux from a porous material during the steady-rate drying period is typically higher than that of a free water surface, owing to the additional contribution of surface roughness to the effective evaporative surface area. Thus, the drying rate is affected not only by the environmental conditions (RH, T, air speed), but also by the sample porosity, specific surface area, and degree to which the surface is saturated with water (Tournier *et al.* 2000).

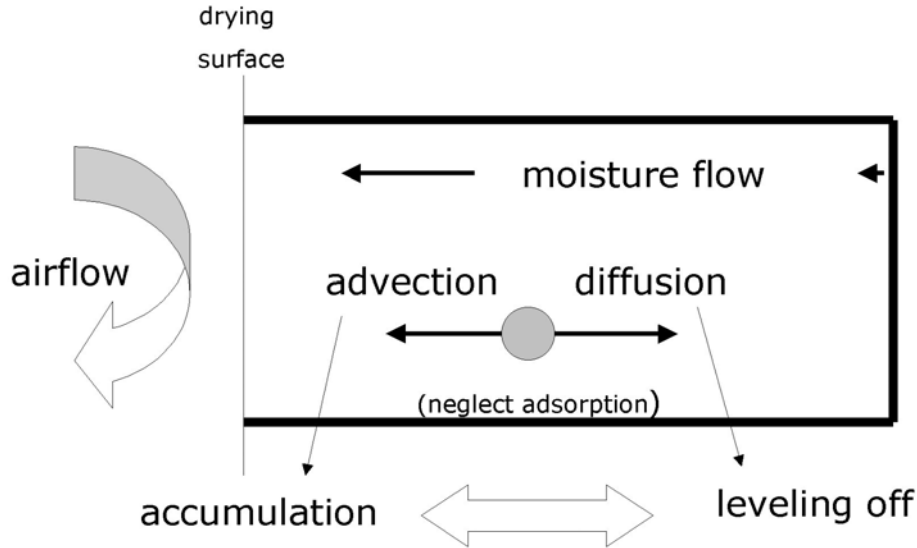


Figure 1: A schematic diagram of the one-sided drying of a sample saturated with a salt solution.

During the second period, the pattern of liquid water migration is affected by the porous structure of the material due to different capillary forces exerted by pores of varying size. Where micropores are interconnected with macropores, water is preferentially drawn into the micropores due to capillary pressure gradients, while the surface macropores begin to empty of liquid water. Consequently, water near the receding drying front starts to form isolated clusters, capillary flow becomes discontinuous and transport occurs through the vapor phase. The water clusters evaporate due to the large difference in relative humidity between the air near the clusters and that at the surface of the material. During drying, air will invade the largest pores, where the capillary pressure (P_c) is lowest, as can be seen from the following equation:

$$p_c = \frac{2\gamma}{r_m} \cos(\varphi) \quad (1)$$

In this equation, r_m is a pore radius that discriminates between the pores filled with water ($r < r_m$) and the empty pores ($r > r_m$). γ [Nm^{-1}] is the surface tension of the liquid/vapor interface and φ is the contact angle between the liquid/air and liquid/solid interface. With increasing moisture content the radius of the widest pore just filled with water, r_m , increases and therefore p_c decreases. If gravity is neglected, the moisture transport during the drying can be described by a non-linear diffusion equation [Bear and Bachmat 1990]:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D(\theta) \frac{\partial \theta}{\partial x} \right) \quad (2)$$

In this equation θ [m^3m^{-3}] is the volumetric liquid moisture content, $D(\theta)$ [m^2s^{-1}] is the so-called isothermal moisture diffusivity. In this 'lumped' model all mechanisms for moisture transport, i.e., liquid flow and vapour diffusion, are combined into a single

moisture diffusivity, which depends on the actual moisture content. Here, the transport of water due to a salt gradient has been neglected.

For the transport of salt by water two mechanisms can be identified. This first one is diffusion, a well-known example of which being the spreading out of a drop of ink in a glass of water due to Brownian motion. Diffusion has the tendency to level off any accumulations, but in porous materials is a rather slow process. The second mechanism for ion transport is advection—a good example of which is the transport of pollutants in a river, the flow of the water carrying the pollutants downstream. As such advection can be an effective means of ion transport, and is generally much faster than diffusion. In a porous material there will always be a competition between advection and diffusion. If the adsorption of ions onto the pore walls is neglected, the ion transport can be described by [Huinink *et al.* 2002]:

$$\frac{\partial (\theta c)}{\partial t} = - \frac{\partial}{\partial x} \left(\theta \left(D_c \frac{\partial c}{\partial x} - c U \right) \right) - R \quad (3)$$

In this equation c [mol l^{-1}] is the ion concentration in the water, D_c [m^2s^{-1}] is the diffusion coefficient of the ions in the moisture in the porous medium, U the water velocity [ms^{-1}] and R [$\text{mol l}^{-1} \text{s}^{-1}$] a term reflecting the crystallization rate. The term θc represents the total salt content in the porous materials, whereas the first term on the right hand side describes the diffusion and the second the advection of the ions by the moisture flow.

The competition between advection and diffusion is illustrated in figure 2, which shows the change in salt concentration during drying of a sample saturated with a 3M NaCl solution, measured non-destructively by nuclear magnetic resonance (NMR) [Pel *et al.* 2002]. It can be seen that within 1 day after drying starts, the Na content develops a peak just below the drying surface, showing that during the initial drying, Na ions are advected to the surface (position 0 mm). At the surface, the NaCl concentration slowly increases to 6 M (its saturation value). At this point any additional advection will result in crystallization, which was indeed observed in the form of a white efflorescence on top of the sample. As the surface is changed by the salt, the drying conditions change and the rate of advection decreases. From this point on, i.e., in the order of 3 days, the NaCl concentration profile in the sample starts to level off due to diffusion until the total sample is at 6 M. At 12 - 15 days after the start of the drying process the Na profiles are flat again and the total sample is at 6 M.

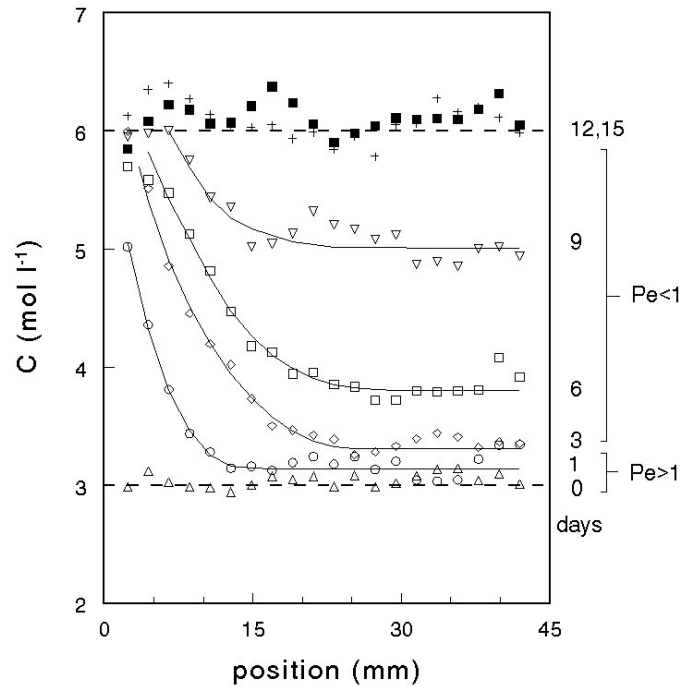


Figure 2. NaCl concentration profiles measured using NMR during drying of a fired-clay brick sample of 45 mm length after 0, 1, 3, 6, 9, 12, and 15 days. The drying surface is at 0 mm.

The competition between advection and diffusion during drying can be defined in terms of the Peclet number [Huinink *et al.* 2002, Pel *et al* 2002, Pel *et al* 2005]:

$$Pe \equiv \frac{U L}{D_c} \quad (4)$$

where L [m] is the length of the sample, D_c [m^2s^{-1}] is the ion diffusion coefficient, and U the water velocity [ms^{-1}]. Hence, for $Pe \ll 1$ diffusion dominates and the ion-profiles will be uniform, whereas for $Pe \gg 1$ advection dominates and ions will be accumulated at the drying surface. In figure 2 we have also indicated the Pe number at the drying surface, and as can be seen initially Pe is larger than 1. But as soon as there is crystallization at the surface Pe drops to below 1. Therefore, the Peclet number is a means of summarising these various processes within a single model, thus giving a single value to describe the tendency for accumulation at the surface.

Concerning salt transport, crystallization and subsequent damage there are still many unresolved questions, of which we will only discuss a few:

2.2 Effect of solution properties

The importance of solution viscosity as a factor in determining the rate of liquid water transport, and hence the ultimate location of salt deposition was clearly demonstrated by Kotter and Riekert [1978], and more recently by Ruiz-Agudo *et al.* [2007]. It was found that increased solution viscosity due to increased ionic concentration reduced the rate of capillary flow, and enhanced the recession of the evaporation front. The deposition profile of the salt altered from the majority of the salt being accumulated at

the surface, to a more homogeneous distribution throughout the depth of the material and subfluorescence.

Importantly, the surface tension of the solution, and its ability to wet the pore walls also alters with ionic concentration. This has a dramatic effect on the rate of capillary flow. Furthermore, the contact angle of a salt solution is enhanced compared to pure water, and so the ability of the solution to wet the pore surface is reduced [Garrecht *et al.* 1988]. This has also been shown by Sghaier *et al.* in the case of sodium chloride to result in the formation of thick films, which can contribute to salt transport via a phenomenon similar to salt creep within the porous structure [Sghaier *et al.* 2006]. However, this effect appears to be dependent on the salt type. While the salt creep behaviour observed by NaCl tends to wet the surface and lowers the critical moisture content of a material severely, another salt such as Na₂SO₄ has almost no effect. Consequently, an increase in the ionic concentration can cause significant changes to the properties of a saline solution, and thereby affect the deposition pattern of salts.

2.3 Support structure effects

In heterogeneous layered objects (such as wall paintings, polychrome sculpture, and masonry), it is often observed that salts originating from one layer give rise to damage in another layer. This is due to the transport of salt by advection from one layer into the other, and is related to the pore sizes of the different materials. On drying, the material with the smallest pore size—and hence the largest capillary pressure—will hold moisture the longest. Indeed, it has been shown that even when the fine porous material is at the surface, and the coarse porous material is underneath, the material with the coarse pores will dry first [Petkovic *et al.* 2007, Diaz Goncalves *et al.* 2007]. In this situation, salts are advected from the coarse porous material to the fine porous material. Indeed, this is the intended function of a desalination plaster. In the reverse situation, where the coarse porous material lies on top of the fine porous material, the coarse porous material again will dry first. However, in this case, the fine porous material beneath remains wet, and ions are transported to the interface where they accumulate. Hence, it is clear that the success or failure of a desalination plaster is dependent on the relative pore size of the plaster vs. the substrate. Moreover, in addition to capillary discontinuity, salt crystallisation may also be promoted at junctures within the object's stratigraphy by a local increase in pore size, which has been shown to reduce the threshold supersaturation of the salt solution [Putnis *et al.* 1995]. This is reflected in the case of wall paintings, where salts are frequently observed to accumulate and crystallise between layers in the object stratigraphy [Cather 2003a].

2.4 Boundary conditions

The boundary conditions at an air/material interface can be formulated as:

$$q_v = \beta(h_a - h_l) \quad (5)$$

where β [kg m² s⁻¹] is the mass transfer coefficient and h_a the relative humidity of the air and h_l the relative humidity of the air/fluid in the porous materials. This last term is derived from the sorption isotherm (also called the hygroscopic curve). The transfer coefficient depends on many parameters, such as air velocity, thickness of the

boundary layer above the drying surface and the porosity of the material. But in the presence of salt, the situation gets even more complicated as both the mass transfer coefficient and the sorption isotherm are a function of the salt content [Rijniers 2004]. These boundary conditions will determine if crystallization occurs as subflorescence or efflorescence, but until now there are still no models, which can predict this for a given material, salt content and drying conditions.

2.5 Crystallization damage

The first scientific study of the relationship between salt crystallization and pressure was undertaken by Lavalley, and published in 1853. In this paper experiments indicating the ability of salts to push away a certain weight are described. In 1916, Taber showed that a crystal present in a saturated solution is able to lift a certain weight. In 1949, Correns finally came up with a mathematical model to calculate crystallization pressure. He showed that the solution in contact with the crystal has to be in a supersaturated state in order to derive a crystallization pressure, [Correns 1949, Goudie 1997] which is given by:

$$P_c = \frac{nRT}{v_c} \ln\left(\frac{C}{C_o}\right) \quad (6)$$

where P_c is the crystallization pressure, C the saturation concentration in the pore, C_o the concentration in the bulk solution, v_c the molar volume of the salt and n the number of the ions in the salt. In recent years further work, notably undertaken by Scherer, Flatt and Steiger, has lead to a refinement of the model proposed by Correns [Flatt *et al.* 2007]. However, although correct, this model was shown by Rijniers *et al.* 2005 to only account for high pressures in very small pores (<10 nm). Therefore, the real mechanism behind the crystallization damage in historical materials, which typically have much larger pores, is still not known. Moreover, other issues relating to the various crystallization behavior exhibited by different salt types, and the role of salt mixtures in the development of damage are still not resolved.

3. Practical considerations

Although preventive conservation is the preferred option where possible, nonetheless treatments are sometimes necessary. Whilst conservators try to use proven materials and methodologies, practical guidance regarding their selection and application is often not available. In respect to salt reduction treatments, if no reasons to the contrary are known, conservators will tend to opt for affordable materials that have good working properties, although these may not be the most effective.

By raising a series of notional questions relating to salt reduction interventions, we are compelled to consider both conservation practice and scientific understanding. The following questions, therefore, serve to provide a basis for discussion of aspects of both our current state of knowledge and to highlight the requirement for further scientific and conservation research:

- How should one go about evaluating salt deterioration problems?
- What sort of samples need to be taken and why?
- Is the mechanical removal of efflorescences always beneficial?
- Should conservators adapt their poultices and application methodologies to suit every object?
- Should one pre-wet before applying a poultice, and how much water should a poultice contain?
- How long should one leave a poultice, and should the poultice be removed before it dries?
- To what depths do poultices work?
- Is knowing what salts have been removed in a poultice sufficient?

3.1 Evaluating the problem

How should one go about evaluating salt deterioration problems?

Despite the development in recent years of increasingly sophisticated models for salt/moisture transport processes in porous media [Karoglou *et al.* 2007], their application in the conservation field is extremely limited. These models are primarily intended for use by the building industry, and use material parameters known for standardised modern building materials. However, these do not apply to the heterogeneous aged materials found in historic buildings. Moreover, the level of complexity allowed within such models is insufficient to accurately reflect the diverse material composition and structure of real objects, and the fluctuating environmental conditions to which they are typically exposed. Importantly, none of the models available at present are able to simulate combined salt and moisture transport for mixed salt systems. Consequently, such simulations are no substitute for rigorous site-based observations and study. Investigations must, therefore, be based on the specific object, and not on generalised assumptions.

At present, site assessments are often carried out in a rather *ad hoc* fashion, the accuracy and usefulness of which are largely dependent on the expertise of the investigator. It has been shown, that if undertaken in a more structured manner according to a series of clearly defined methodological approaches, the usefulness of *in situ* investigations can be dramatically enhanced [Sawdy and Price 2005b, Sawdy 2001]. To this end, a protocol for site-based investigations is needed that is flexible enough to be adapted to the needs of each particular case. To correctly identify the true source of the salt and the nature of the damage mechanisms taking place requires an evaluation of the problem in context, and involves a host of concerted actions, which include the following:

- a liquid moisture survey (see Cather 2003b)
 - examination of original technique and added materials
-

- a condition survey
- environmental monitoring (if required)
- sampling and analysis (if required)
- treatment testing & assessment (if required)

What sort of samples need to be taken and why?

Sample type

Currently, there are no standard methods to investigate the distribution of soluble salts within stone and wall paintings. Various sampling and analytical techniques are used by different researchers, which give very different information. See table 1

Clearly, the type of samples to be taken is determined by the type of information required, and the limitations imposed by the object regarding invasive sampling. In certain instances, qualitative information regarding the type and distribution of salt present can be sufficient to answer questions regarding the nature and source of salt damage. For example, at Hardham church in West Sussex, England, a combination of condition recording, archival research and qualitative analysis using relatively simple techniques was sufficient to identify the source of salts causing severe damage to the C12th Romanesque wall paintings [Sawdy 1994, Sawdy *et al.* 1997, Heritage *et al.* forthcoming]. The salts were identified as primarily gypsum using optical microscopy, and SEM-EDX analysis. However, it was stratigraphic evidence provided by cross-sections that succinctly revealed the source of the salts. The gypsum efflorescence was found to be contained within a layer of wax, which on the basis of historical evidence could be firmly dated to 1934. From the condition survey it could be seen that the spread of the damage matched the previous location of a coal-fired stove (installed during the nineteenth century and exchanged for newer model in 1935) at the west end of the nave until the 1960s. Thus, it is clear that the sulfation problem at Hardham originated from an earlier coal fired heating system (figures 3-5).

Sample type	Impact on object	Analytical Techniques typically used (As reported in literature)	Qualitative information	Quantitative information	Advantages	Disadvantages
Efflorescences	Non invasive	- X-ray diffraction (XRD) - Optical microscopy - Fourier transform Infrared spectroscopy (FTIR) - Merck water test kits - Atomic absorption spectroscopy (AAS) - Inductively coupled plasma atomic emission spectroscopy (ICPAES) - Ion chromatography (IC)	YES	AAS, ICPAES, IC only	Mineralogical identification Non invasive	May not reflect salt composition subsurface
Poultices	Non invasive	- Atomic absorption spectroscopy (AAS) - Merck water test kits - Inductively coupled plasma atomic emission spectroscopy (ICPAES) - IC	YES	semi-quantitative only	Non invasive	May not reflect salt composition of object, due to solubility constraints
Ion exchange resins	Non invasive	- X-ray fluorescence (XRF) - IC	YES	semi-quantitative only	Non invasive	Solubility constraints. Risk of chemical alteration of original materials
Cross sections	Invasive	- Optical microscopy - Scanning electron microscopy-energy dispersive x-ray analysis (SEM/EDX) - Micro FTIR - Histochemical tests	YES	semi-quantitative only	Distribution in relation to stratigraphy	Non quantitative Invasive
Micro drillings	Invasive	- ICPAES - IC	YES	YES	Good quantitative data	Invasive. Does not give mineralogical identity of solid phases
Cores	Invasive	- AAS - ICPAES - IC - Ion selective electrodes - filter photometry - flame photometry - hygroscopic moisture content (HMC)	YES	YES	Good quantitative data (except for HMC method: semi quantitative only)	Highly invasive.

Table 1. Approaches to salt sampling



Figure 3: Hardham Church, West Sussex, England: General view of nave (photo: A. Heritage, Conservation of Wall Painting Department, Courtauld Institute, 1997)



Figure 4 A-C: Hardham Church, West Sussex, England: Detail of wall paintings: showing damage due to salt crystallisation and organic coatings (photo: A. Heritage, Conservation of Wall Painting Department, Courtauld Institute, 1994)



Figure 5. Hardham Church, West Sussex, England: Photomicrograph (200x magnification) of cross section taken from nave south side, after histochemical test for sulphate. Gypsum (identified by areas stained purple) is present solely within a yellow layer of wax (dated to 1934) between the original plaster and a surface limewash dated to 1935. (photo: A. Heritage, Conservation of Wall Painting Department, Courtauld Institute, 1994)

However, in other situations, it is necessary to undertake invasive sampling to quantitatively determine the salt distribution through the depth of the object. This is most typically required to investigate the pathways of salt and moisture content within the object, and/or assess the efficacy of salt reduction treatments, to which end drilled core samples are normally taken. However, here again, one encounters significant variation in sampling methodology. Many researchers in the field of stone and architectural conservation favour a somewhat coarse sampling interval of the region of 5-10 cm at the surface, the depth interval increasing as sampling proceeds further into the object. However, for layered objects, such as wall paintings and polychrome stone, discrete stratigraphic information is required. The salt distribution varies significantly through the outermost layers of the object, which are in the order of a few millimetres thick [Cather 2003a, Sawdy and Price 2005b]. When it is suspected that the salt damage is environmentally activated, it is desirable to assess the behaviour of the salts present in relation to relative humidity and temperature. In such situations it is clear that investigations should focus on the salt distribution within the zone of damage. Therefore, if the problem is primarily located at the object's surface (which it most typically is), detailed information of the salt distribution within the first few millimetres is needed. Moreover, sampling should reflect material construction of the object (e.g. plaster layers). Thus, it is necessary to adjust the depth interval between sample segments according to the type and material construction of the object, the deterioration phenomena observed, and the intended purpose of sampling.

Sampling strategies

When investigating salt deterioration problems, it is important to take into account, and to differentiate between, the many factors that can exert an influence on the pattern of salt distribution and damage observed (Arnold 1985, Arnold 1991), which include:

- the sources of salt and moisture supply
- the structure and composition of the porous support,
- the composition of the salt mixture present,
- the environmental conditions to which the object is exposed
- the conservation history of the object

This requires from the outset of the investigation a coherent sampling strategy, which takes into account the various factors under investigation, and also the levels at which these factors are to be assessed (Sawdy and Price 2005b). This is not particularly onerous, but certainly requires clarity of thought. This approach offers significant advantages in the extent to which the data can subsequently be interrogated, and is greatly facilitated by a few simple techniques:

- A consistent sampling methodology: i.e. the samples are all taken in the same manner;
 - A balanced design by which the factors under investigation are assessed at different levels (e.g. treated vs. untreated, damaged vs. undamaged), with the same sampling procedure applied to each;
 - When undertaking quantitative analysis, replicate sampling (i.e. taking more than one sample from each location) should be included to provide a means of estimating the degree of error within the data. It should be stressed that each
-

and every sample need not be replicated, and the number of replicates should relate to the overall number of samples taken.

The use of replicate sampling for site assessments is not particularly widespread, however, this technique provides valuable information as it allows proper assessment of the significance of variations between samples (i.e. are the differences observed real or just due to background error?), and so is not as wasteful as it might initially appear. Due to ethical restrictions, a balance has to be sought between minimising the number of samples, and gaining reliable data. Invasive sampling is only justified if it will yield adequate information—if the data set is so small that it is critically flawed (e.g. important factors have been overlooked, or it is not possible to determine if variations in the results are significant) then sampling should not have been undertaken.

A well thought out and balanced sampling strategy, therefore, offers two significant advantages:

- it saves a significant amount of time and effort (in terms of taking and analysing the right samples);
- collected data can be subsequently evaluated using statistical methods.

3.2 Interventions

Following an adequate assessment of the object (as set out above), decisions can be made regarding the most appropriate approach towards alleviating the problem. Currently, the options available for the mitigation of salt problems fall into either of two categories: *passivation* by means of environmental control, or by conversion to less soluble (and hence in theory less damaging) salts (Matteini 1991); or *reduction* by means of transporting salts away from the zone of deterioration—ideally removing them from the object. Clearly, for this second category, which is dominated by the use of mechanical removal typically in combination with aqueous methods (with or without the added inducement of pressure, or electrical means), salt and moisture transport plays an important role. This paper is concerned with salt reduction methods, and consequently passivation methods such as environmental control, although valid—and in some cases preferable to reduction methods—will not be discussed here. Moreover, the difficulties inherent to aqueous salt reduction of porous materials (and in particular wall paintings) have already been rehearsed (Cather 2003a, Heritage *et al.* 2006).

Is the mechanical removal of efflorescences always beneficial?

As an adjunct to aqueous salt reduction treatments, salt efflorescences are typically first removed by mechanical means. Indeed, in certain situations, which preclude the introduction of water, mechanical removal may be regarded as a desirable alternative to aqueous salt reduction. However, while this is commonly regarded as a relatively non-invasive intervention, nevertheless, the removal of efflorescences can also affect salt and moisture transport processes behaviour:

- (1) It has been shown that the mechanical removal of salt efflorescences can affect the thermodynamic behaviour of the remaining salts (Sawdy and Price 2005b). At Cleeve Abbey it was observed that the predicted thermodynamic behaviour
-

of salts within the wall plaster altered when efflorescences composed of niter (KNO_3) were omitted from the mixture. The upper limit of relative humidity under which the salt mixture underwent crystallisation and deliquescence fell from around 90 %RH to below 70 %RH without the efflorescences. Meanwhile, the recorded environmental conditions fluctuated primarily between 80-90 % RH. Consequently, it was concluded that mechanical removal of the efflorescences could not only reduce the amount of salt present in the vicinity of the paint layer, but also manipulate the thermodynamic behaviour of the remainder such that phase transitions become less likely (figure 6).

- (2) It has also been observed that the formation of efflorescences can influence the evaporation rate, typically leading to an increase in the drying rate, while efflorescence removal was observed to decrease the drying rate (figure 7). A similar observation was also recently reported by M. Prat at the CRYSPOM meeting, Paris 22-23 May 2008 [Prat 2008]. Investigations undertaken as part of the EU Saltcontrol project also indicated that this effect might be dependent on the efflorescence morphology, since it was informally observed that while the development of open fern-like efflorescences with a high surface area enhanced the evaporation rate, the formation of compact surface crusts had the opposite effect.

While in general the mechanical removal of efflorescences is still to be recommended, and indeed provides a useful means of monitoring further salt activity (in conjunction with documentation), nevertheless, the practical implications of these findings warrant further investigation. Moreover, in terms of salt and moisture transport, in general it is still not known for a given porous material which conditions will give rise to efflorescence or subflorescence. Consequently, the decision to mechanically remove efflorescences, and the scheduling of such interventions should take into account the following:

- the removal of efflorescence can affect the thermodynamic behaviour of salts in relation to environmental conditions
 - the salt efflorescence itself is a porous layer and can influence the drying behaviour of the object
 - the salt efflorescence can act as a sacrificial layer through which the growth front is progressively removed further away from the object surface.
-

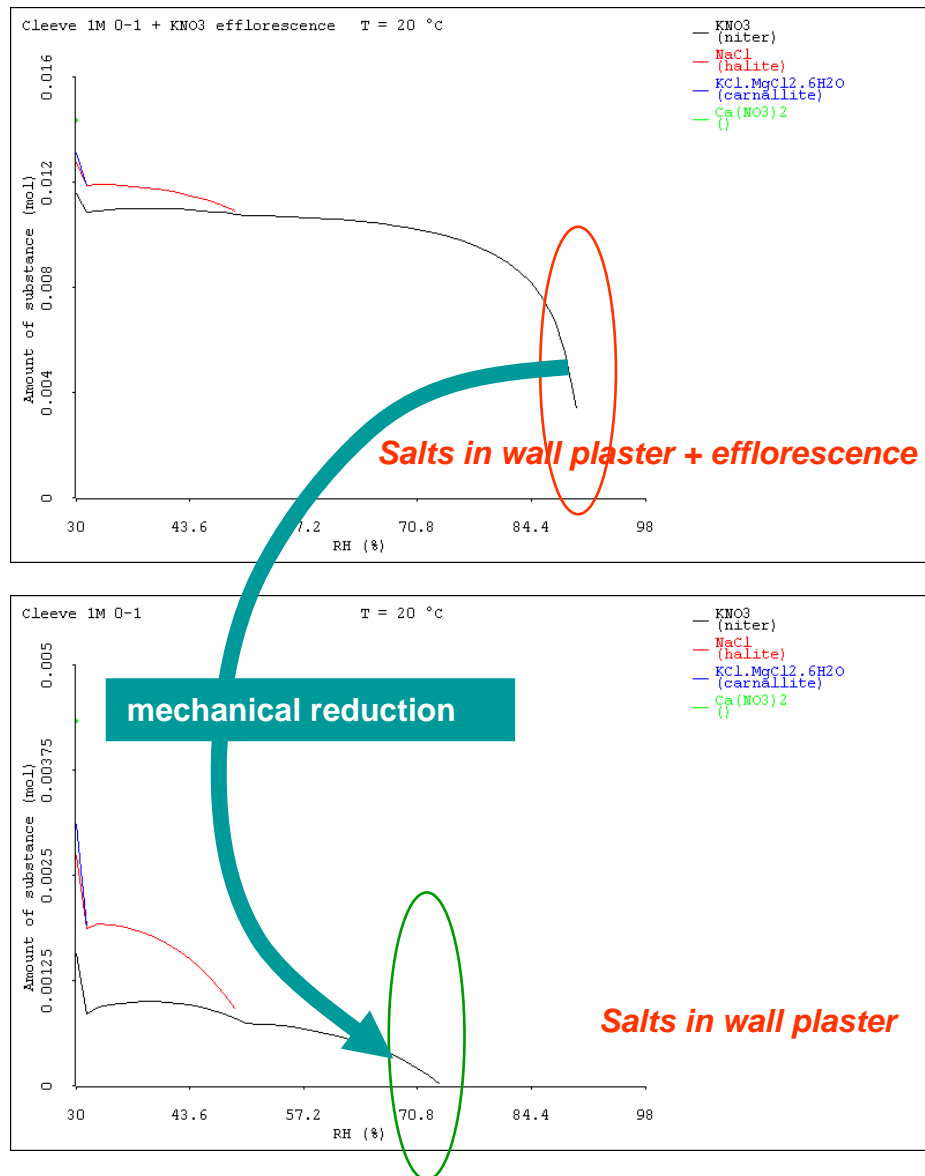


Figure 6. Influence of salt efflorescence removal on thermodynamic behaviour

Effect of inhibitor treatment, airspeed and efflorescence removal on drying of NaCl contaminated sandstone after 48 hours

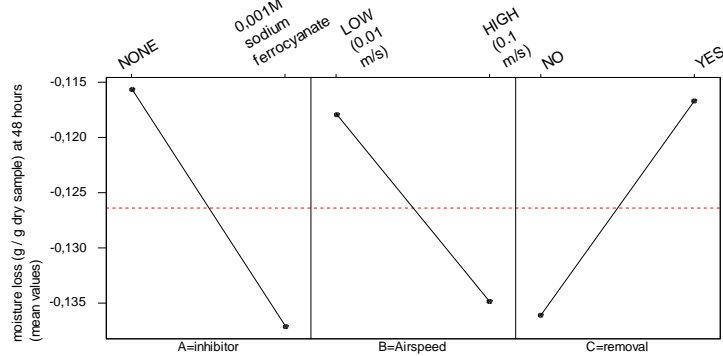


Figure 7: Influence of salt efflorescence development on drying behaviour. All samples: Prague sandstone (4cm diameter, 3cm length); NaCl 1% (by weight); RH = 50%; T = 20 C. Factors tested: A = inhibitor treatment; B = airspeed; C = efflorescence removal. Method: samples were dried, contaminated by capillary rise, the sides and base sealed with wax film, and exposed to the test conditions. The mass was recorded at time intervals over four days. Efflorescences were routinely removed by mechanical means from a proportion of the samples according to the experimental design.

The results (as summarized in this graph) showed that:

- the use of sodium ferrocyanide promotes the evaporation rate of NaCl solutions (most probably related to increased formation of efflorescences)
- increased airspeed results in increased evaporation rate of NaCl solutions
- efflorescence removal slows evaporation rate of NaCl solutions

Should conservators adapt their poultices and application methodologies to suit every object?

It could be argued that the issue of removal and clearance of poultice materials and possible use of an intervention layer to protect a vulnerable paint layer—typically Japanese tissue—is the main concession conservators make to the substrate. However, depending on the mechanism of transport of desalination the pore size distribution of the poultice should also be taken into account:

- in the case of desalination by diffusion (wet poulticing) it is only the salt concentration gradient which is determining the process. As such this method will always work regardless of the substrate vs. poultice pore size distribution, but this is a very slow method of desalination and typically only applied on smaller objects, which can tolerate prolonged exposure to moisture.
- In the case of desalination based on the much faster transport mechanism of advection (drying poultice) the pore size distribution of the poultice in relation to the substrate is of importance. In order to have advection from the substrate into the poultice, the poultice must have smaller pores than the object. Consequently, the poultice will dry out last.

Therefore, in theory it would be preferable if conservators were able to tailor the poultice (in particular its pore size distribution) to the specific requirements of the

substrate. However, to date practical evidence of extent to which salt extraction efficiency is affected by the substrate/poultice pore size relationship is limited. Consequently, this issue is currently undergoing investigation as part of the EU Desalination project. This raises two subsidiary questions:

- How can we easily and effectively determine the porosity characteristics of an individual object?
- How can we easily and effectively determine the porosity characteristics of an individual poultice?

To determine the pore structure of a material requires invasive sampling and laboratory analysis, and is therefore time consuming and expensive. Moreover, the pore size characteristics of most poultice materials are not known. This is in part due to inherent difficulties associated with measuring the pore size distribution of materials that are deformable, and have a tendency to contract on drying. Moreover, for the majority of poultice materials (particularly cellulose pulps) their porosity is a function of their moisture content, and hence they need to be characterised when wet. However, most of the characterisation methods (e.g. mercury intrusion porosimetry (MIP)) currently available are only suited to dry materials. A notable exception to this is the use of NMR, which can be used to measure the pore size distribution within wet materials.

In view of this lack of information, as part of the EU Desalination project, work is currently underway to characterise the pore structure of a range of commonly applied poultice materials using both wet and dry methods (MIP and NMR). However, this is only one half of the problem, since what is really needed is a simple and reliable way (preferably on site and non invasive) to establish the compatibility of the poultice to the substrate. Correspondingly, the Desalination project is also focussing on this issue with the aim of developing a test method to help tailor the selection of poultices to suit the individual needs of the object.

Should one pre-wet before applying a poultice, and how much water should a poultice contain?

Pre-wetting and poultice moisture content are important issues. However, as yet there are no hard and fast answers. The amount of water required is dependent on the type, amount and distribution of the salts, the porous structure of the object, the prevailing environmental conditions (RH, T and airspeed), and the desired aim of the intervention. Typically, the aim is to extract salts from as deep within the object as possible, however, whether this is indeed beneficial to the object, or results in long lasting mitigation of salt damage is not known.

The more water that is introduced, the greater the depth of penetration, and hence mobilization of salts. However, given the negative impact large quantities of moisture may have on water sensitive materials (e.g. binders, pigments etc.), and the risks of transporting salts further into the object, the option to pre-wet and the moisture content of the poultice has to be decided on a case by case basis.

Nevertheless, it has to be acknowledged that pre-wetting has several functions in addition to the dissolution of the salts. Following mechanical cleaning of the surface

to remove dirt, debris and salt efflorescences, pre-wetting also serves to flush clean the surface, thus aiding the application of an intervention layer and poultice, and improving their conformity and adherence to the object.

Clearly, this is an area where more research is needed to identify ways in which the quantity and depth and rate at which water is introduced to the object can be better controlled, possibly through the use of specifically designed poultices rather than water sprays. The key aim is to introduce sufficient water to dissolve the salt, but at the same time, avoid advecting salt deeper into the object. In this respect not only the amount, but also the rate at which water is introduced plays an important role. It has been suggested by Wendler [pers. Comm.], that a quick on-site test for conservators to assess the amount of water required within the poultice to achieve a desired penetration depth against a given standard would be advantageous.

How long should one leave a poultice in place, and should the poultice be removed before it dries?

The application time of a poultice is strongly dependent on which transport mechanism is dominant. In the case of diffusion-controlled 'wet poultices' it is important to keep the salt content in the poultice as low as possible in order to maintain the concentration gradient. Moreover, as mentioned above, diffusion is a relatively slow process. Hence, one has to reapply the poultice often over a very long time (month/weeks rather than days). By contrast, in the case of advection-controlled 'drying poultices', the initial first drying period where salts are mobilised by liquid transport is important. Consequently, one should apply the poultice for as long as this transport mechanism is dominant. This will generally be in the order of days. Indeed, overly long application times for drying poultices run the risk of diffusion rather than advection becoming dominant, resulting in back diffusion of salt from the poultice into the object.

These considerations are somewhat at odds with the WTA Merkblatt [2003], which recommends the following:

- for wet poultices 5-10 days with 4-6 repetitions;
- for drying poultices 3-6 weeks with 2 repetitions.

Clearly, this is an area, which warrants further research. Again, the development of a simple on site test method, to evaluate the moisture and salt content of the poultice over time would help conservators identify when (for wet poultices) the poultice should be exchanged, and (for drying poultices) advection ceases.

3.3 Evaluating the effect of interventions

Once the decision has been taken to undertake mechanical removal of efflorescences and/or an aqueous salt reduction treatment, it is clear that the potential impact of such interventions needs to be evaluated. Two aspects in particular warrant close attention: salt redistribution, and the selective extraction of salts.

To what depths do poultices work?

The primary aim of a salt reduction treatment is to transport salts away from the zone of damage, ideally removing them from the object. However, it is clear that in practice this is only partially achievable. Recent research, undertaken as part of the EU FP6 Desalination project, has shown that the depth of extraction using poultices on porous materials such as stone and clay fired brick is generally of the order of only 20mm. Moreover, this work has also shown that at depths beyond 20mm, there is a net accumulation of salt (figure 8). Consequently, it is clear that the direction in which salts are mobilised, and where they are transported to, is relatively uncontrollable, and at best can only be described as a partial removal—hence rendering the use of terms such as ‘desalination’ questionable as an accurate reflection of what is actually achieved [Leitner 2003]. This may seem a question of semantics, but nevertheless is of significance, particularly in relation to what we as conservators like to believe we are achieving, and also client expectations.

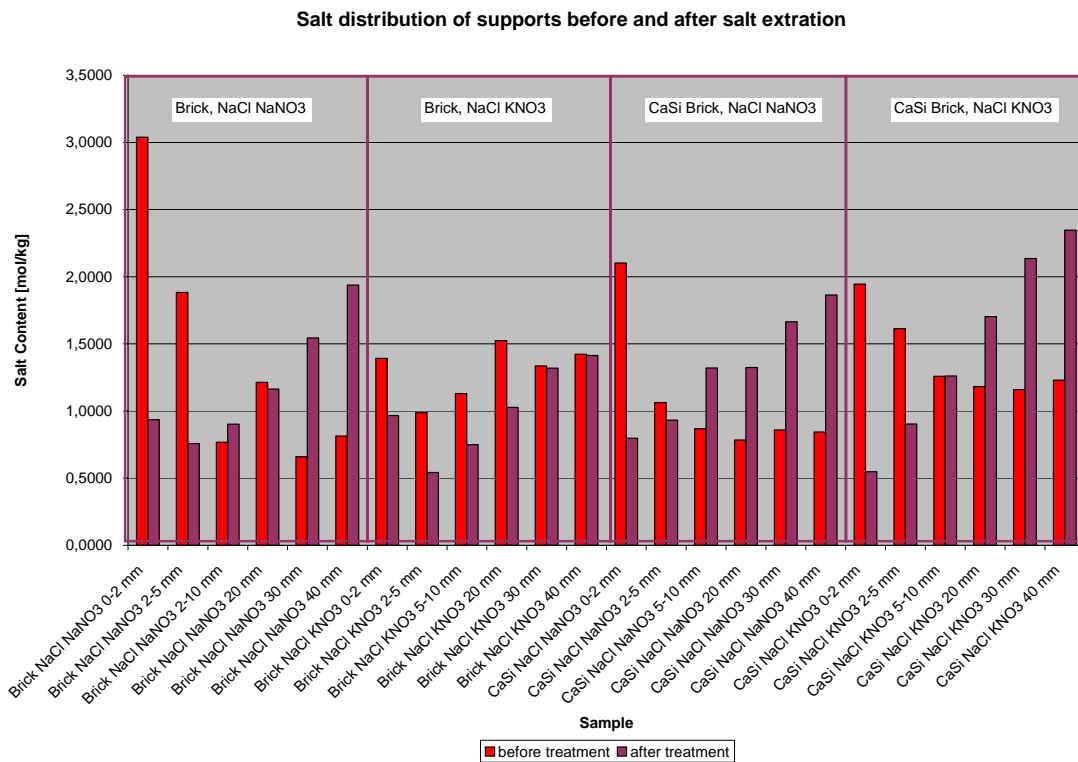


Figure 8: Surface extraction vs. accumulation at depth following aqueous extraction by poulticing.

For this experiment, the following factors were tested:

Factor	- level	+ level
RH	85%	50%
Support	Brick	Calcium silicate brick
Saltmix	NaCl/NaNO ₃ (1:1 by moles) 0,5 saturation	NaCl/KNO ₃ (1:1 by moles) 0,5 saturation
Poultice	Cellulose BC1000:BW40 (1:1) water content = 5	Kaolin/sand (1:5 by weight) water content = 0,2
Pre-wetting (2L/m ²)	Yes	no
Intervention layer	Yes	no

The dried porous supports were contaminated with either of the salt solutions by capillary rise, and freeze dried for 1 week to achieve a reasonably homogeneous salt distribution (as seen in the graph). They were then subjected to aqueous salt extraction, according to the experimental design given in the table above for a period of 2 weeks. Drilled core samples taken after poulticing were analysed by ion chromatography (Dionex ICS 90). The post treatment results shown here are presented in the form of mean average values for the entire data set (38 experimental runs, 228 samples).

Is knowing what salts have been removed in a poultice sufficient?

The short answer to this question is “no”. There is a tendency to evaluate the success of desalination treatments in terms of the amount of salt extracted, while insufficient attention is paid to the post treatment behaviour of residual salts. In addition to issues of re-distribution and accumulation at depth of remaining salts, the thermodynamic impact of aqueous reduction treatments should also be considered. The ranges of relative humidity and temperature responsible for activating cycles of salt damage are dependent on the composition of salts present, so it is clear that this behaviour can potentially be altered through preferential extraction of salts. Indeed, there is evidence to suggest that salt reduction may in some cases cause increased damage as a consequence of selective extraction [Cather 2003a, Weber *et al.* 1992, Weber *et al.* 1996, Leitner 2003].

Recent work, undertaken as part of the Desalination project has investigated this issue in more detail, and preliminary results show that selective extraction does indeed occur, and can cause significant changes in pre- and post treatment salt behaviour. Moreover, the current findings indicate that the effect appears to be dependent on the salt mixture composition and support type (figure 9). At present, the underlying causes of this effect are not known, since it is clear that it is not solely due to solubility constraints, but that perhaps to some degree, ion exchange or differences in ion mobility may play a role. Further work, planned as part of the Desalination project, will study this effect on a wider range of support types and salt systems, to elucidate the underlying reasons for this behaviour, and to investigate if the post treatment behaviour of residual salts can in any way be pre-determined. Nevertheless, it is clear that the potential effects of selective salt extraction should be considered prior to carrying out a salt reduction treatment—particularly so in the case of objects with sensitive surfaces such as wall paintings.

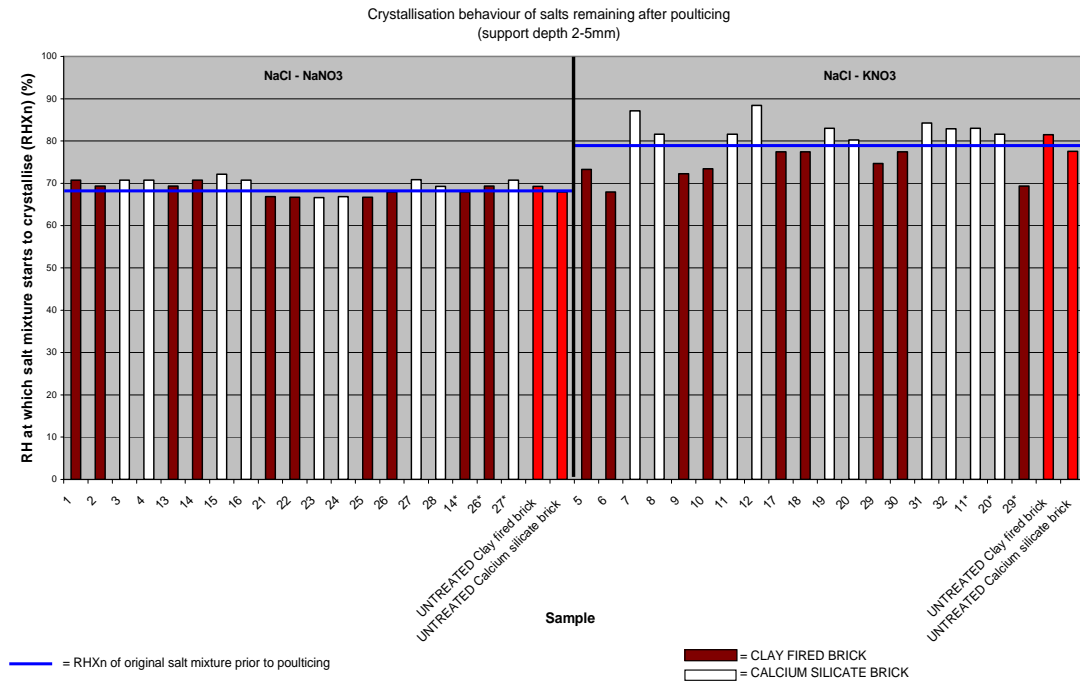


Figure 9A. Selective extraction of salts

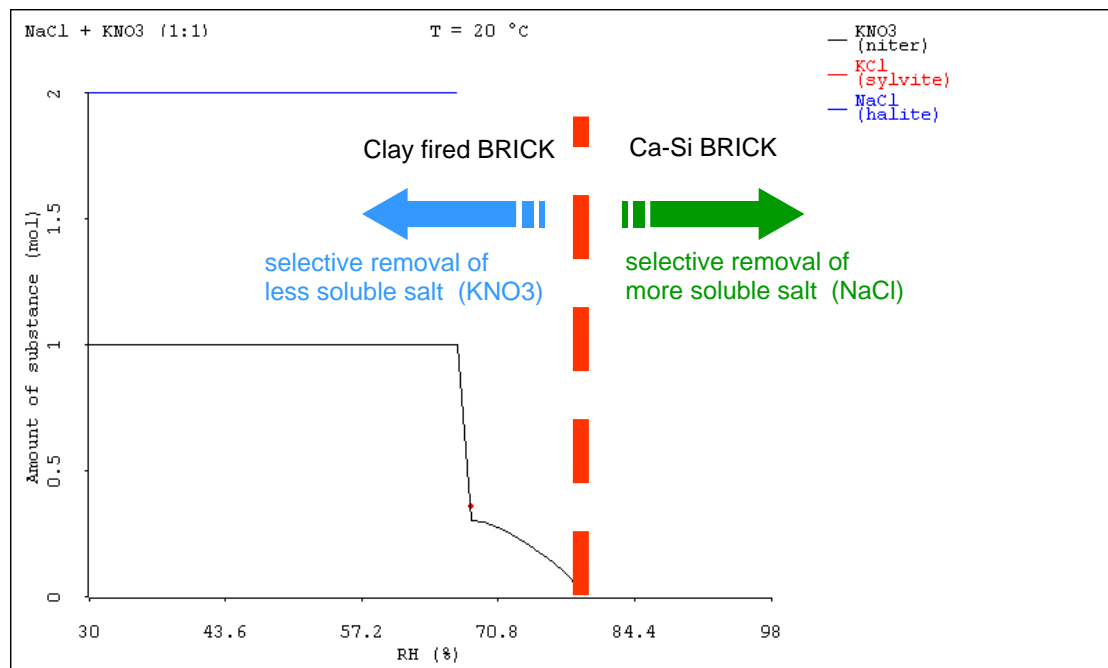


Figure 9B: *Selective extraction of salts: effect of support type on NaCl-KNO₃ mixture*
 The data presented here originates from the aqueous extraction experiment described in figure 8. The results from the IC analysis were analysed using the Environmental Control of Salts (ECOS) programme to predict the RH value (RHxN) at which the salt mixture within each sample would start to crystallise at 20 degrees C. Statistical analysis was undertaken to determine the significance of the various experimental factors tested. This showed that (at the 99% probability threshold) *selective extraction was significant depending on the salt mixture and support type*. From figure 9A it can be seen that while the NaCl-NaNO₃ mixtures do not show any significant alteration in salt behaviour post treatment, the NaCl-KNO₃ mixture

does. Figure 9B: summarises the effect due to the different supports: for the clay fired brick samples preferential removal of KNO_3 resulted in a decrease in RHX_n , while for calcium silicate brick samples preferential removal of NaCl resulted in an increase in RHX_n of the mixture.

4. Conclusions

The above discussion has shown that our current understanding of the transport processes involved in salt damage is incomplete, and highlights the need for scientifically-founded practical guidance for conservators. Furthermore, we need to improve the methods by which we assess and conserve salt deteriorated objects. There are things we can start to do to improve this situation, not only through high-end scientific research, but also through the development of simple test methods by which the conservator can tailor the poultice mix to suit each case, and gauge its function *in situ*. Moreover, a fundamental change is needed in the way in which we approach salt problems; not only in the methods we use, but also in relation to our perceived goals. A key point in the mitigation of salt deterioration problems is the transport of salts away from the region of damage—whether by removal or re-distribution. The evidence presented above shows that aqueous salt reduction often results in only a partial and relatively superficial removal of salts (and is hence perhaps more a maintenance procedure than a definitive solution to the problem). Consequently, we need to focus our attention less on the total amount of salt removed, and more on the distribution and behaviour of the residual salts. Information regarding the actual long-term outcome of the majority of treatments undertaken is simply not known, due to a general lack of post treatment assessment—an area that has been woefully neglected. A greater awareness is needed, therefore, of the importance of pre- and post treatment assessment, and the benefits to be gained thereby—particularly so that the information obtained can feed back into conservation research. Moreover, in the scheduling of conservation investigations, sufficient time should be allowed for the useful assessment of trial test areas (Tabasso and Simon 2006).

Notwithstanding the importance for an increase in conservation funding in general, it is nonetheless crucial that conservation managers distribute available funds judiciously between treatment-based and preventive conservation measures. As the relevance of implementing long-term monitoring programs gains wider acceptance, it is not acceptable to expect conservators and scientists to undertake such work at their own cost. Therefore, funds need to be made available to allow assessment of the outcome of both past treatments and preventive interventions; to learn from these measures, and thereby improve the efficacy of future treatments and preventive measures.

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