RELATIONSHIPS BETWEEN SALTS AND CONSOLIDANTS IN DECAYED STONE

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Abstract.

This thesis considers in depth the relationships between salts commonly found in decayed limestones and sandstones, and consolidants used to treat the stone.

The first section discusses the sources of salts in stone, and reviews current theories on the mechanisms of salt-related decay. The problem of salts in stone can be treated in various ways; attempts may be made to remove the salts, or the salts may be stabilised in situ. Different desalination and stabilization techniques used by conservators, including consolidation, are reviewed, and their advantages and disadvantages are discussed.

The next section considers in detail the possible interactions between salts and consolidants in stone, in the light of recent research. There are three stages during treatment of stone with a consolidant when salts and consolidants may be affected by each other. These stages are initial application of the consolidant; curing of the consolidant, as it changes from liquid to solid; and the period after the consolidant has cured and is a solid inside the stone. For each of these stages, the practical observations of conservators are discussed, and the theoretical situation is examined in detail. Questions are raised about physical encapsulation of salts by consolidants, and salt movement in consolidated stone.

The next section attempts to answer some of the questions raised. This is achieved by conducting experiments examining the encapsulation of salts by consolidants. Scanning electron microscopy is used to discover whether salts are coated by consolidants, and whether the consolidant is able to inhibit salt activity when the treated salt is subjected to extremes of humidity. The experiments determine that only one of the consolidants tested will form a flawless covering over the salts. Furthermore, salt activity in fluctuating humidities is not prevented by any of the consolidants. In treated stone samples,

however, the rate of salt movement is retarded by the presence of a consolidant.

The final chapter takes into consideration the experimental results and combines them with the literature review to summarize the information. Some theoretical situations involving salts, consolidants and stone are discussed, drawing upon the information presented. Finally, recommendations are made for future research into salt movement in stone after consolidation.

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To my Mum and Dad

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1. INTRODUCTION.

This thesis has been written to broaden our understanding of one small, but important, area relating to stone decay and its conservation. There is an immense body of literature available on ~~the~~ stone decay, and on treatment methods to prevent further deterioration.

A major area of research has concentrated on the deterioration of stone. Just as stone is a complex material consisting of a wide variety of minerals in different matrices, so there are many different ways in which the stone may deteriorate over time. It is accepted that the presence of soluble salts in stone is a major problem. The exact mechanisms of stone decay due to salt action are the subject of a large body of current research. It is realised that salts produce a large amount of damage in stone. To counteract the problem, a number of different treatment methods have been developed.

Despite numerous reports on the success of treatments, very few studies have researched the interactions between the salts and consolidants. Conservators have observed that salt action has continued in some instances despite treatment (for example Bradley & Hanna, 1986; Larson, 1980). In the past five years there has been an increase in research into how salts affect the polymerisation processes of some consolidants (for example Danehey et al., 1992: Kumar & Price, 1994). However, there has been no study examining the overall relationships between salts and consolidants both during and after treatment of affected stone.

This is an important area of research for a number of reasons. As stated above, it has been observed that salt activity has increased in some treated stone objects (Bradley & Hanna, 1986) despite desalination and consolidation. This raises an interesting possibility that consolidants are in some way mobilizing salts, in direct contrast to the aims of the conservation treatment. How are the salts being mobilized and transported to the surface of the stone? If salts are influencing the polymerisation of consolidants, how does this affect the overall performance of the consolidant inside the stone? Does salt contamination affect where the consolidant cures inside the stone? After consolidation, how and where do salts move to?

The aim of this thesis is to examine in depth the relationships occurring between salts and consolidant inside decayed stone. It is necessary to understand how these two parameters affect each other so that treatment of stone can be achieved effectively. During the course of this dissertation, the interactions between salts and consolidants both during and after consolidation will be studied in detail. There are three main stages to be examined - initial entry of consolidant into salt-contaminated stone, curing of the consolidant, and the period after consolidation. For each of these stages, practical observations will be related to theoretical considerations. Experiments to help answer some of the questions raised will be undertaken. In the final chapter, the data presented in the preceding chapters will be analysed and conclusions drawn about the relationships between the salts and consolidants discussed.

This study has been limited to that of the relationships between salts and consolidants in stone. However, the principles discussed and the information presented can be applied to the treatment of any salt-laden porous material.

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2. THE PROBLEM OF SALTS IN STONE.

Before attempting to discuss the relationships between salts and consolidants, it is important to understand the sources~~,~~ and types of salts found in stone. These subjects will be examined in the following chapter.

2.1 SOURCES OF SALTS.

If a stone has a soluble salt problem, it is important to know how the salts have been introduced into the stone. There are three main sources of salts:

a. the salts may be present in the original material of construction;
b. the salts are added to the stone from extraneous sources;
c. the salts are formed from the stone's constituents.

2.1.i Salts inherent in original material.

Some salts may be present from when the stone was originally formed. For example, if a rock was formed in a marine environment, it is possible that evaporite minerals may have been deposited in the rock. A list of common evaporite minerals is given in table 2.1. These minerals are deposited in a specific order of increasing solubility, with the least soluble mineral being laid down first. Of the minerals listed, a number are commonly found in analyses of decayed stone (e.g. Arnold, 1976; Feilden, 1982; Arnold et al~~,~~,1986).

Livingston cites the presence of evaporite minerals in a sandstone used for a chapel in Auburn, USA, as the cause of the stone's decay (Livingston, 1994). The decay had previously been attributed to the limestone over sandstone effect, but this did not fully explain the types and locations of decay. (The limestone over sandstone effect occurs when salts ~~gypsum~~ formed from an overlying course of limestone leach~~es~~ into the underlying sandstone and recrystallize~~s~~, leading to decay of the sandstone.) Analysis of samples of the stone (see appendix 1), combined with the alveolar decay pattern and the origin of the sandstone led to the conclusion that the salts were deposited in the stone during its original formation (Livingston, 1994).

Mineral name	Formula
Anhydrite	$CaSO_4$
Bischofite	$MgCl_2.6H_2O$
Bloedite	$Na_2Mg(SO_4)_2.4H_2O$
Carnallite	$KMgCl_3.6H_2O$
Epsomite	$MgSO_4.7H_2O$
Glaserite	$K_3Na(SO_4)_2$
Gypsum	$CaSO_4.2H_2O$
Halite	$NaCl$
Hexahydrite	$MgSO_4.6H_2O$
Kieserite	$MgSO_4.H_2O$
Kainite	$KMgClSO_4.11/4H_2O$
Leonite	$K_2Mg(SO_4)_2.4H_2O$
Polyhalite	$Ca_2K_2Mg(SO_4)_4.2H_2O$
Sylvite	KCl
Thenardite	Na_2SO_4

Table 2.1 Common evaporite minerals (From Livingston, 1994).

2.1.ii Salts from external sources.

Many salts are introduced by water. Groundwater dissolves soluble salts from the surrounding earth to produce a dilute salt solution. If an object lies in the ground for a period of time, this solution will percolate through the object, depositing some salts inside the stone. Groundwater is drawn up structures in contact with the ground by capillary absorption. This process manifests itself as 'rising damp'. The groundwater may rise 3 to 4 metres above ground level (Arnold et al., 1986). The types of salts deposited will depend upon the composition of the ground through which the water has percolated. For example, in regions with limestone geological formations, high carbonate concentrations will be found. High nitrate levels may be attributed to agricultural effluents (Riederer, 1971). High chloride levels could be expected in saline regions. At the Temple of Karnak in Luxor, Egypt, high levels of chlorides, and traces of nitrates were present in the decayed stone walls (Saleh et al., 1992).

The salts are deposited as water from the solution evaporates. They crystallise from solution in a particular order, with the least soluble salt being deposited first. In this way, zones containing different types of salts are formed. Arnold and co-workers (1986) analysed the types and distribution of salts on the surfaces of walls inside the Müstair Convent, Switzerland. Nitrates and chlorides, which are highly soluble salts, were concentrated in the upper zone of rising damp, whilst the soluble sulphates were concentrated in the lower region (Arnold et al., 1986).

A further source of salts may enter the stone from other building materials. One example is the introduction of sulphates from Portland cement. Portland cement was used for repair work on stone sculptures at the Victoria and Albert Museum, London. However, the alkali salts in the cement were transferred into the sculpture, leading to severe spalling of the original surface (Larson, 1980).

The specific use of stone, for example as part of a salt storage building (Riederer, 1971) may be responsible for high concentrations of salts in the stone.

2.1.iii Salts formed from the original material.

The other major source of salts is those formed from decay of the stone itself. Included in this category are salts formed from acid attack, and biodeterioration of stone.

A major body of research has concentrated on the effects of airborne acidic pollutants on the alkaline materials in stone (see for example Cooke et al., 1993). The main pollutants are carbon dioxide and sulphur dioxide. Although carbon dioxide occurs naturally in the atmosphere, in urban areas its concentration is increased as a result of the combustion of fossil fuels (Cooke et al., 1993). When dissolved in rainwater, carbonic acid is formed, which reacts with carbonates of calcium and magnesium to produce a more soluble hydrogen carbonate (Torraca, 1984). Calcium sulphate dihydrate (gypsum, $CaSO_4.2H_2O$) is the usual product formed from the reaction of sulphur dioxide with calcitic materials on stone surfaces (Torraca, 1984; Cooke et al., 1993). Sulphur dioxide may be deposited directly onto the surface or when dissolved in rainwater as sulphuric acid. The possible routes via which gypsum may be formed on stone are shown in figure 2.1.

When sulphur dioxide concentrations were greater than 50 parts per billion in the atmosphere, the sulphation effect probably dominated stone dissolution (Cooke et al., 1993). However, with reduced sulphur dioxide emissions, carbon dioxide plays a more important role. Concentration levels of nitrogen oxides have increased in conjunction with the increasing number of cars on the roads. In principle, stone may be attacked by nitric acid formed from the dissolution of nitric oxides in water or water vapour. However, calcium nitrate, although very soluble, is not found in high enough concentrations in the run-off water from rainwashed stone to suggest significant nitrate attack of stone (Cooke et al., 1993). However, nitrates have been recorded as present in Egyptian limestone artifacts at the British Museum (Bradley & Hanna, 1986). A possible role of nitric oxides may be as catalysts. Although there is experimental evidence of nitrogen dioxide, and ozone enhancing the absorption of sulphur dioxide on stone samples, field studies in the United Kingdom have not corroborated the laboratory results (Cooke et al., 1993).

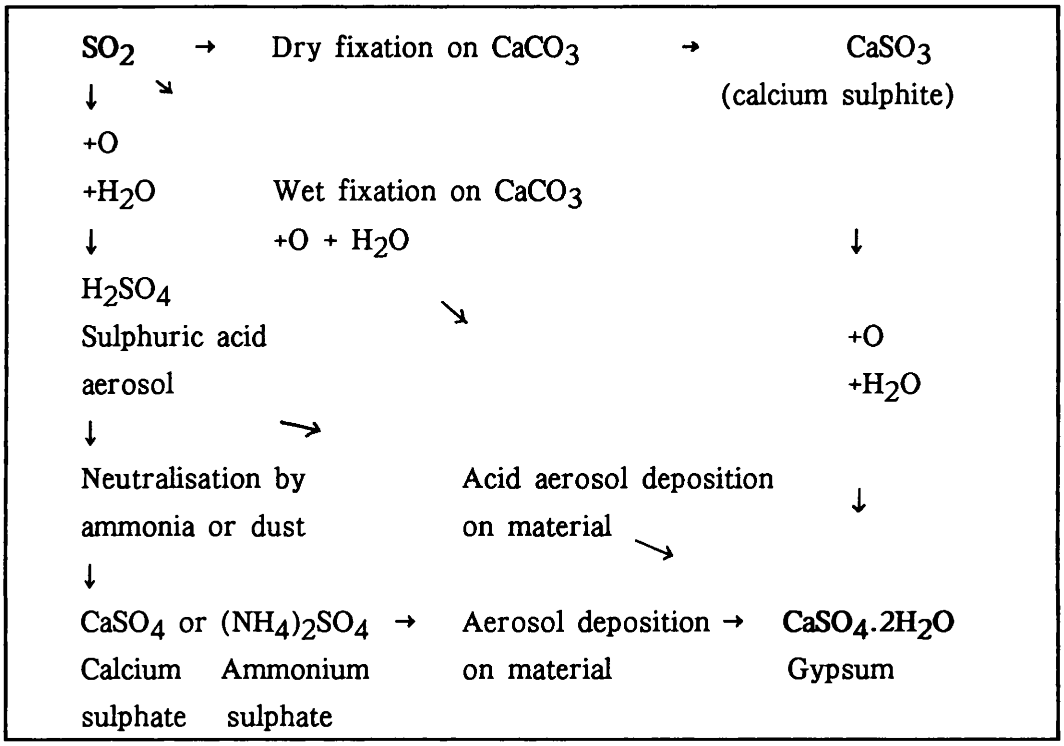

Figure 2.1 Possible reaction mechanisms for formation of gypsum from sulphur dioxide. (From Torraca, 1984.)

Stone is also affected by the acids formed by biological agencies. The following is a brief summary of some aspects of biodeterioration relating to the formation of salts. A full review of the literature on biodeterioration of stone is presented by Griffin et al. (1991).

Biochemical deterioration is defined as "the direct action by biological organisms' metabolic processes on the substrate" by Griffin et al. (1991). Some organisms excrete acids and water-soluble organic chelating agents, which react with the host stone. The acids are excreted to form water-soluble metal chelates which the organism can then utilise as nutrients (Ganorkar et al., 1987), or to directly attack the stone and facilitate a firmer hold on the stone. Endolithic algae produce acids to dissolve carbonates to enable penetration into the substrate (Griffin et al., 1991). The use of the salts produced for nutrition leads to depletion of basic cations in the stone. The salt produced is dependent on the type of acid, and the host stone. Fungi produce a range of organic and inorganic acids, including oxalic, lactic and gluconic acids. The type of acid produced by bacteria is species-specific. For example, sulphur-oxidising bacteria convert hydrogen sulphide into sulphuric acid, whereas nitric acid is produced indirectly from bacteria in the nitrogen cycle. Since lichens are a self-sufficient association of fungi and algae, or cyano-bacteria, the acids formed and the resulting salts will depend upon the original constituents of the lichen. Some organisms produce acids as a by-product of living. Carbon dioxide from respiration of lichen reacts with water held at the surface by the lichen's thallus to produce carbonic acid (Griffin et al., 1991).

It can be seen that many of the decay products are similar to those formed by other decay mechanisms (for example the formation of sulphates by sulphur-oxidising bacteria). The importance of microbial degradation has therefore been difficult to ascertain, since it may easily be overlooked as a cause of decay. The formation of salts characteristic of biodeterioration has sometimes been attributed to other sources. For example the presence of calcium oxalate patinas was assigned to previous conservation treatments (Fassina & Borsella, 1993). It is thought that biodeterioration is a secondary degradation process, whereby biological populations establish themselves after some decay has already occurred (Griffin et al., 1991; Riederer, 1984; Winkler, 1971). The biological agents then act in synergy with other decay processes, thus exacerbating stone degradation.

Previous conservation treatments are, unfortunately, also responsible for the formation of salts in some situations. In an investigation into the decay of the Donatello Pulpit in Prato Cathedral, conservators discovered that a previous consolidation using fluorosilicates had contributed to the problem. The fluorosilicates had reacted with the limestone, resulting in formation of soluble salts and decohesion of the stone (Franchi et al., 1978).

2.2 MECHANISMS OF SALT DETERIORATION.

The manner in which salts cause decay is as varied as the range of salts present in the stone.

2.2.i Salt formation.

When salts are formed from the original stone, for example gypsum from calcite, the product of decay may be of a different size and crystalline structure than the reactant. If the molar volume of the salt is larger, the increase in size in a confined space may create stresses on the surrounding stone matrix. If the product is smaller in size, a void will be left, creating a weakness. If the salt formed is soluble and is removed in solution, again a void will be left in the structure. Solution loss is a problem more characteristic of calcitic stones (Smith et al., 1991). In a sandstone with calcitic cement, solution loss of the binder leads to granulation of the surface of the stone, with loss of the main constituents of the stone, even though these particulates have not themselves deteriorated. The salt formed may also exhibit a different rate of thermal expansion, creating stresses within the stone with variations in temperature.

2.2.ii Salt hydration and crystallisation cycles.

Individual salts.

The major concern regarding soluble salts is their action under fluctuating environmental conditions once deposited inside the stone. When the relative humidity (RH) and temperature fluctuate, the composition and structure of the salt/ water system changes (Puehringer & Engström, 1985). Salts respond to the changes either by crystallising from or going into solution. The RH at which this transformation occurs is specific for each individual salt, and is known as the equilibrium RH of the salt. A list of the equilibrium RH's of common salts is given in table 2.2.

Ammonium chloride	80%	Ammonium nitrate	66%
Calcium chloride	33%	Calcium nitrate	56%
Magnesium chloride	34%	Magnesium nitrate	53%
Potassium chloride	85%	Potassium nitrate	94%
Sodium chloride	75%	Sodium nitrate	75%

Ammonium sulphate	81%
Calcium sulphate	99.96%
Magnesium sulphate	90%
Potassium sulphate	98%
Sodium sulphate	93%

Table 2.2 Equilibrium RH's of some salts at 20°C (from Price & Brimblecombe, 1994).

The growth of a salt crystal from solution in a confined pore space creates stresses on the pore walls. The strain of repetitive solution and crystallisation cycles damages the pore walls. In a similar manner, the changes in volume exhibited by a salt with multiple hydration states under fluctuating environmental conditions stress and damage the pore walls inside stone. These reasons are generally given to explain how salts cause stone decay (eg Torraca, 1984). However, the above explanation is a gross over-simplification of the situation. There are numerous factors influencing the actions of the salts, including volume change, rate of change and type of crystal formed. Crystallisation, dissolution, hydration and dehydration are different processes that need to be assessed individually.

To illustrate the complexity of the situation, the case of sodium sulphate will be discussed. Sodium sulphate exists in multiple hydration states, two of which are commonly found in decayed stone - thenardite (anhydrous sodium sulphate) and mirabilite (sodium sulphate decahydrate). [The heptahydrate form of sodium sulphate is assumed to ~~rarely~~ occur rarely in stone, because the thermodynamic conditions governing its formation do not generally develop under normal conditions inside stone (McMahon et al, 1992).] Sodium sulphate is considered one of the most damaging salts because its hydration and crystallisation cycles occur at temperatures and RH's commonly experienced in temperate regions (Arnold, 1976; Arnold et al., 1986; Feilden, 1982). The simplistic view is that the volume increase as thenardite hydrates (up to 3% (McMahon et al., 1992)) damages the stone. However, not only is the transformation of thenardite to mirabilite not a simple case of hydration, but also the shape of crystal formed is dependent on initial conditions (Doehne, 1994). It has now been demonstrated that thenardite is converted to mirabilite not by hydration, but hydration-through-solution, whereby the thenardite first dissolves in solution before mirabilite is precipitated from the super-saturated solution (McMahon et al., 1992). Thus hydration is a two-part process (Pühringer & Weber, 1990). Moreover, the particle size formed differs depending upon the conditions of formation. This was observed under the environmental scanning electron microscope by Doehne (1994). He observed that an initially large crystal of mirabilite dehydrated to form sub-micron particulates of thenardite. This particulate mass was highly porous, with a large surface area. Subsequent humidity fluctuations resulted in this mass alternating between the anhydrous and decahydrate forms of sodium sulphate, but retaining the sub-micron form, with the large surface area. Only with the introduction of excess liquid water to dissolve this pariculate mass completely, and subsequent evaporation of the water, did a large crystal of mirabilite form, with well-defined crystal faces. The importance of these observations with respect to decay inside stone can be seen when referring back to the original model of decay (see for example Torraca, 1984). This model assumes a large crystal forms, but this only occurs when excess water is present. At other times, a sub-micron particulate mass forms. The large surface area of this mass allows it to react quickly to changes in RH and temperature. However, because of its highly porous nature, any volume changes are accommodated by the voids in the structure, thus theoretically preventing pressure from building up inside stone (Doehne, 1994). In contrast, the rapid crystallisation of large crystals of mirabilite may not give stone a chance to accommodate the stresses created. If volume change were slower, the force generated may not be delivered with the same impact, allowing dissemination of any stresses created before damage occurs.

From the above, it appears that hydration cycles of the sub-micron particulate mass may not be as damaging as crystallisation cycles involving sodium sulphate (Doehne, 1994). Pühringer & Weber (1990) state that the dehydration of hydrates "always results in very small particles". They also state that no hydration, and hence no hydration pressures occur when such anhydr~~a~~ite particles are in contact with a concentrated salt solution. However, when the salt hydrates are in contact with sub-concentrated solutions (ie excess water), hydrates occur as "thin, tight salt films". Pühringer and Weber summarise that the effect of salt hydrates is due to the "moisture-related behaviour of thin cement-like films or volumes of anhydrate particles, combined with the effect of partial hydration/ dehydration (but not crystallisation) processes" (1994). This notion of excess water needing to be present for hydration is similar to

Doehne's observations. However, Pühringer and Weber appear to be discussing all salts, and not a single case. It is dangerous to extrapolate the findings for sodium sulphate, and apply them to all other salts, since salts react differently in different situations.

Mixed salts.

Prevention of salt cycles by stabilising the environmental conditions (either keeping the RH lower, or higher than the equilibrium RH of the salt thereby keeping the salt permanently dry or permanently in solution) would therefore appear to be a logical tactic in the limitation of salt decay (Puehringer and Engström, 1985). Since the equilibrium RH's of individual salts are known (see table 2) the task of finding a suitably low, or high RH may appear to be relatively easy. However, this approach to the problem does not take into account the synergistic effects of salts in a salt mixture. A good example of this is the change in equilibrium RH from their norms produced by mixing sodium chloride and sodium nitrate in solution. The point at which salt crystallises out of solution is lower than would be expected (Price and Brimblecombe, 1994). It is possible that many other salt mixtures produce similar effects that have as yet to be studied. When determining environmental controls for decayed stone, it is therefore important to not only analyse the salt content, but to take samples and cycle them in order to find a suitable environment at which the salts present are not active.

Another example of salts working in synergy to damage stone is the effect of sodium chloride on the solubility of gypsum. Chlorides are often mentioned in lists of salts present in decayed stone (Bradley & Hanna, 1986; Larson, 1980; Saleh et al., 1992). Their role in the decay process appears to be as a secondary force, increasing the effects of other salts. They may act as a catalyst in the acid attack of sulphur dioxide on stone (Cooke et al., 1993). Sodium chloride also affects the solubility of gypsum, and can reduce the RH at which gypsum crystallises out of solution (Price and Brimblecombe, 1994). Referring to the model by Arnold et al. (1986) depicting the zones of salt crystallisation, sulphate crystallisation is shown in the lower zone. However, analysis of the water soluble ions reveals two sulphate peaks, one in the lower zone and one in the upper zone, the same region as the nitrates and chlorides. In a later article, Zehnder indicates that gypsum in the higher zones is quite a common phenomenon (Zehnder, 1993). Zehnder then suggests that hygroscopic salts may be "essential for mobilising gypsum as they give rise to an increased water sorption and thus a generally higher water content of the substrate" (Zehnder, 1993). In a separate article, Baggio supports this, stating that the presence of hygroscopic salts can "introduce a substantial increase of equilibrium moisture content" (Baggio et al., 1993). Thus the stone surface will be wetted more frequently, and other salts will be in contact with water more frequently than if the deliquescent salt were not present (Livingston, 1994). Sodium chloride (and other evaporite minerals) also affects the ionic strength of the salt solution, intensifying the cycles of dissolution and crystallisation (Livingston, 1994). Livingston also states that evaporite minerals affect the physical form of the gypsum crust. Arnold & Zehnder noted that in the lower zone of rising damp, a hard, compact layer of gypsum formed, which changed to a powdery coating in the upper zone (where hygroscopic salts were present) (Zehnder, 1993).

2.3 SUMMARY.

The ways in which salts interact is as complex and varied as the the manner in which they cause decay to the stone. It is important to learn more about these processes so that treatment of the effects can be more effective. The type and physical state of salts inside stone affect the success of consolidation processes.

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3. TREATMENT OF SALT-CONTAMINATED STONE.

There are two options available to limit the destructive action of salts on stone. The first is to remove the salts from the stone; the other stabilization of the salts in situ.

3.1 DESALINATION OF STONE.

Desalination of stone involves removal of soluble salts by dissolution. When choosing a desalination technique, various factors need to be considered including whether removal of the salts will reduce the mechanical properties of the stone, and whether the treatment will influence the aesthetic appearance of the stone (Skibinski, 1985). For small objects, desalination in water baths is a possible option. The object is immersed in successive deionised or distilled water baths, and the salt concentration of the water monitored until it is lowered to an acceptable level. This process relies upon the diffusion of the salts in solution from inside the object to the surrounding water bath. It has been suggested that, to accelerate the diffusion process, an electric current can be used (eg Jedrzejewska, 1971; Skibinski, 1985). In experiments using semi-permeable membranes and an electric current, Skibinski demonstrated that salts can be effectively removed (Skibinski, 1985). However, there was no standard desalination technique without the aid of an electric current included in the experiments, making direct comparisons between the two forms of treatment difficult. A novel treatment suggested by Minder-Heng et al. (1994) involves the use of microwaves. In experiments, artificially salted stone samples were subjected to microwave treatments whereby the samples were dried in the microwave. Between each treatment, the samples were soaked in water baths (Minder-Heng et al., 1994). The conclusions reached were that desalination using the microwave is possible. However, the microwave does not facilitate actual removal of the salts from the stone; it only increases the speed of drying of the stone after desalination. Analysis of the methodology and results suggests that the salts are lost during soaking between microwave treatments. In addition, the technique is unsuitable for ~~all~~ some stone types, producing fissures in one of the stones tested (Minder-Heng et al., 1994).

A more commonly used desalination technique involves the use of poultices. The full practicalities are described by Ashurst and Dimes (1990). The basic idea is as follows: the surface to be cleaned/ desalinated is fully wetted. To minimise calcite dissolution in the water, lime chippings should be left to soak in the water before it is applied to the surface (Livingston, 1992). A poultice (usually a clay such as attapulgite or sepiolite) is then applied to the surface in a thin layer and left to dry. As the poultice dries, salts in solution from the wetted area are drawn into the poultice, where they crystallise out. The dried poultice is then removed. The depth of salt removal is dependant on the depth of water penetration. Bradley and Thickett (1992) found that water from poultices penetrated stone to a depth of 20mm. It is advised by most authors that the poultice should be allowed to dry completely before removal (Jedrzejewska, 1971; Ashurst &Dimes, 1990; Skibinski, 1985). To minimize calcite solubility Livingston advises that poultices should be made as airtight as possible, which rules out the practice of allowing the poultice to dry out before removal (Livingston, 1992). Slow drying is necessary to allow salts in solution to travel to the surface of the stone and produce efflorescence rather than subflorescence.

Another poultice technique involves the application of a sacrificial render to the surface of the stone. The salts crystallise on the surface of the render, or between the stone and the render, causing the render to spall rather than the stone. Renders have the added advantage that any external pollutants react with the render instead of the stone surface (Ashurst & Dimes, 1990).

Poulticing is the most practical way of salt removal in large stone objects. Salt is only removed from the outer layers, however, and deeper salt levels remain untouched. Action must be taken to prevent future salt penetration before desalination. Salts deep inside the stone may be activated during desalination, hence repeated desalination processes may be necessary. Ashurst & Dimes (1990) advise against cleaning by soaking in case salts deep within the stone are disrupted. One must consider, however, how deep into the stone water vapour from the atmosphere will penetrate, and activate salts remaining after poulticing of a stone surface.

3.2 STABILISATION OF SALTS IN SITU.

3.2.i Environmental control.

Because of the multitude of ways in which salts may enter stone, and the limited efficiency of desalination, it may not be possible to fully eliminate salts from stone. It is therefore advisable to seek ways of inhibiting their activity. One possible method is to control the environment the stone is subjected to. The salts create problems when fluctuating around their equilibrium relative humidities (RH's), therefore control of the environment to keep the salts either permanently in solution or permanently dry should prevent problems. This may be achieved by controlling the temperature and RH at a suitable level (Pühringer & Engstrom, 1985). Theoretically this appears an attainable objective for an indoor environment, since the equilibrium RH's of individual salts are known. However, as explained in 2.2.ii, salt mixtures do not behave as expected and choosing a suitable RH and temperature at which the salts are inactive is a difficult task.

3.2.ii Chemical interactions.

Pühringer and Engström (1985) used combinations of salts to potentially beneficial effect. They introduced salt mixtures into stone samples in order to stabilise the RH at a level in which the salts are inactive. In theory, this may appear to be an acceptable solution to the problem. However, there are practical limitations to the technique. Questions need to be answered about how to introduce the salts to a depth suitable to prevent their subsequent removal in solution, and how they will react when subjected to pollutant attack. As Price & Brimblecombe pointed out (1994), the effects of two salts on each other may be radically altered by the addition of a third salt. It is thus dangerous to add a salt without thoroughly investigating its effects on all salts present.

Another technique that has been employed is the introduction of a material that reacted with the stone to produce a less soluble mineral than the original stone matrix. An example of this type of treatment is the ~~B~~baryta treatment advocated by Lewin and Baer (1974) whereby sulphates are converted into less reactive carbonates within the stone. The disadvantages of this system are that the salts formed are of a different physical structure and do not attach themselves to the other minerals in the stone. Recently, the conversion of calcium carbonate into calcium oxalate by treatment with ammonium oxalate has been suggested as a protective treatment for wall paintings (Matteini et al., 1994). Calcium oxalate is a much less soluble mineral than calcium carbonate, even in acidic conditions. When samples were treated under laboratory conditions, a lining of calcium oxalate a few microns thick was formed. The surface porosity of samples was reduced slightly, and the resistance to attack by ethanoic acid was increased (Matteini et al., 1994). It is debatable how much protection a layer only a few microns deep could provide in a realistic situation. The small change in porosity still allows salt movement to the surface, thereby encouraging efflorescence rather than crystallisation below the surface.

b/

3.2.iii Physical encapsulation.

A third possibility is the encapsulation of salts, thereby denying access of water necessary to activate the salts. This may be achieved by the introduction of a consolidant to the stone. There are two aims when consolidating stone:
- strengthening of weakened areas of stonework;
- encapsulation of salts.

(Bradley, 1985; Pühringer & Engström, 1985; Skibinski, 1989.)

To achieve encapsulation of the salts, the consolidant should ideally produce a lining around the grains of the stone without filling the pores, thus allowing water to leave the stone without affecting the now immobilised salts (Bell & Coulthard, 1988; Hanna, 1984). A variety of consolidants have been applied, in an attempt to fulfil the above criteria. The following is a brief discussion about the main advantages and disadvantages of some of the more popular consolidation treatments used in stone conservation. For more detailed information, the reader is referred to general books on polymers or stone conservation (for example Clifton, 1980; Horie, 1987; Ashurst & Dimes, 1990).

Epoxy resins have been tested and used on different types of stone because of their superior strengthening properties, minimal shrinkage and no harmful by-products upon curing (Kotlík et al., 1983; Wheeler et al., 1991). Epoxies are generally viscous liquids which need to be diluted to ensure good penetration into stone. Munnikendam (1978) advised that the addition of more than 10% of a solvent would cause a deterioration in the properites of the cured product. The disadvantages of epoxy resins greatly outweigh their advantages, however, particularly since it is an irreversible consolidation treatment. Many epoxies degrade upon prolonged exposure to ultra-violet light, leading to yellowing or darkening of the treated area (Down, 1984; Wheeler et al., 1991). Some conservators consider the appearance of stone treated with epoxy resins unacceptable. In a comparison of treatments, Rossi-Manaresi found that epoxies produced an unsatisfactory aesthetic appearance (1984). If applied in a thick coating, epoxy resins block the passage of water and water vapour, producing an accumulation of salts in a layer underneath the treated surface. With repeated salt crystallisation cycles, this layer spalls, leaving a damaged area. Therefore, epoxy resins are not often used for stone conservation.

Acrylic resins may be applied as monomers which are polymerised in-situ, or as pre-polymerised systems in a solvent. The advantage of applying a monomer which polymerises inside the stone is that deep penetration can be achieved before polymierisation (Kotlík et al., 1980). However, there have been problems finding a suitable catalyst to initiate polymerisation. High temperatures may be used, but this is impractical for large or immovable objects. Kotlík and co-workers (1980) achieved their best results with a benzoyl peroxide initiator and a raised temperature. They discovered that the polymerisation process was difficult to control, and the treated stone often cracked. De Witte (1984) concluded that cracking was caused by contraction of the monomer during polymerisation. Because of the unreliability of the treatment, it is not often used.

Acrylic polymers applied in a solvent, for example Paraloid B72 in acetone or toluene, have been used. With these types of polymers successful treatment requires adequate depth of penetration of the liquid before the solvent evaporates. It is important not to apply too thick a coating, otherwise the stone's pore system becomes blocked at the surface. If there is a continuous supply of soluble salts, they will be prevented from moving to the surface of the stone and will crystallise behind the consolidated layer. With repeated salt crystallisation cycles, this layer will spall (Kotlík & Zelinger, 1978).

Another type of pre-polymerised system employed for stone consolidation are silicone resins. These are pre-polymerised silanes. When applied to stone, they provide a coating on the surface that prevents access of water and salt crystallisation cycles. The silicone resins contain two functional groupings useful for their role as stone consolidants. The Si-O groups may become chemically attached to the stone's surface by hydrogen bonding to the surface, whilst the methyl groups ($-CH_3$) impart hydrophobicity (Torraca, 1984). In practice, however, only a thin layer forms on the surface of the stone, with enough spaces between silicone particles to allow the passage of water vapour, which will activate soluble salts (Torraca, 1984). Degradation of the organic groups is initiated by ozone and ultra-violet radiation, reducing the hydrophobic effect of the silicone over time (Mark et al., 1992; Sramek & Kralova, 1981; Torraca, 1988).

A more successful treatment for some types of stone, mainly sandstones, involves the use of monomeric or partially-polymerised silanes which polymerise in-situ. Silanes are monomers derived from silicic acid ($Si(OH)_4$). The replacement of the hydrogen atoms with alkyl groups (C_nH_{2n+1}) creates an alkoxy silane. For example the replacement of all four hydrogens with ethyl groups produces tetra ethoxy silane (TEOS), $Si(OC_2H_5)_4$) The replacement of an hydroxyl group with an alkyl group creates an alkyl alkoxy silane, such as methyl trimethoxy silane (MTMOS, $SiCH_3(OCH_3)_3$). The polymerisation of silanes will be discussed in detail in future chapters. Silanes appear to be suitable consolidants for siliceous stones, because they are capable in principle of being converted from a mobile liquid into a stable inorganic end product that is similar to the original matrix of the stone (Lewin & Wheeler, 1985). However, there is a very complex reaction sequence occurring which is highly dependent upon conditions within the stone (Lewin & Wheeler, 1985; Charola et al., 1984). It was thought that silanes strengthen stone by chemically bonding to the surface and reinforcing grain contacts (Snethlage & Klemm, 1978; Sattler & Snethlage, 1988; Torraca, 1984).

siliceous

Silanes have also been used with acrylic resins dissolved in them. When these acrylic-silane consolidation treatments have been used, conservators have noticed an increase in the consolidative effects compared to the use of silanes alone (Bradley, 1985; Hanna, 1984; Rossi-Manaresi, 1981; Saleh et al., 1992). Nishiura (1987) believes the role of the acrylic resin in the system is to increase the viscosity of the mixture, thereby holding the silane monomer in the pores of the stone and allowing it to polymerise gradually without evaporating out of the stone. In studies using the scanning electron microscope, Wheeler and co-workers discovered an interesting relationship existing between Paraloid B72 dissolved in methyl trimethoxy silane (1992). As the silane polymerises, the B72 separates from the preparation, since it is insoluble in the methanol released from silane the polymerisation reactions. The presence of the B72 produces a silane phase of unconnected spheres rather than the continuous phase formed by neat silane. The B72 and the silane phase had little affinity for each other. In summary, Wheeler suggests that these composite gels may be less suitable for stone consolidation than the individual constituents. This is in direct contrast to the observations of the conservators mentioned above.

A group of consolidants that have gained favourable reviews from Italian conservators are perfluoropolyethers. These are organic polymers applied to stone in a solvent. They produce a transparent solid which is permeable to gases, and does not break down upon exposure to ultra-violet radiation (Frediani et al., 1981, 1982). However, their efficiency as determined by Frediani and co-workers (1981, 1982) was found to decrease over time (Chiavarni et al., 1993). Researchers are now experimenting with amide derivatives, to establish a stronger bond with the surface of the stone (Piacenti et al., 1993).

A relatively new technique designed to control the activity of salts involves the use of membrane technology. The membranes under investigation are thin polymeric films which exhibit preferential permeability to certain gases only. The potential of membranes that selectively prohibit the passage of water vapour through stone has been monitored (Drioli, 1991). To ensure adequate protection of a wall, for example, an intact film covering the pore walls and salts would have to be applied. Drioli (1991) also comments on the membranes' easy removal from surfaces, raising doubts about their durability in an aggressive environment.

3.3 SUMMARY.

From the information presented in this chapter, it can be seen that many varied techniques have been tried to prevent salt activity. These range from removal of the salts to attempts at prevention of their movement. There is no treatment that can be applied to all situations. There are practical problems with many of the solutions.

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4. INTERACTIONS DURING INITIAL APPLICATION OF CONSOLIDANT.

The penetration of a consolidant is dependent upon its ability to wet the surface of the substrate, in this case stone. This wetting ability is controlled by the surface free energies acting at the interfaces between the liquid consolidant, the surrounding air saturated with its vapour, and the solid substrate.

4.1 SURFACE FREE ENERGY.

4.1.i Definition.

In a liquid, molecules that are located within the bulk of the liquid are, on average, subjected to equal forces of attraction in all directions, whereas those located at an interface, for example a liquid-air interface, experience unbalanced attractive forces resulting in a net inward pull (fig. 4.1) (Shaw, 1992).

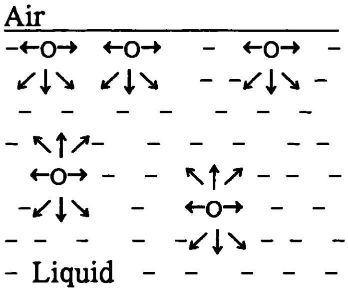

Figure 4.1. Attractive forces between molecules at the surface and in the interior of a liquid.
(From Shaw, 1992.)

As many molecules as possible will leave the liquid surface for the interior and the surface will tend to contract. To form fresh surface, work must be done against the inwardly directed molecular forces in order to pull a sufficient number of molecules from the interior to the surface (Garrett, 1966). This work of formation of a unit of fresh surface is defined as the surface free energy (γ) of the liquid (Garrett, 1966; Shaw, 1992). For pure liquids, the surface free energy can be equated to the surface tension, but this is not the case for solids (Garrett, 1966). When fresh liquid surface is formed, the molecules in the liquid are able to move to redistribute energy evenly. However, when a solid surface is extended, the distance between molecules is increased and the rigidity of the structure does not allow for a redistribution of energy. Therefore the "tension" in a solid surface is greater than the surface energy (Wake, 1982). The surface free energy involves two phases, for example the boundary between a liquid and a solid, or a solid and liquid vapour. There is no general expression for γ that is applicable to any fluid or solid in isolation (Scheidegger, 1974). In this work, it will be assumed that the surface free energy of a liquid is that of the liquid in contact with air saturated with its vapour (γ_{lv}).

Consider a liquid dropped on the surface of a solid (fig 4.2a). The final shape of the drop will depend upon the relative magnitudes of the cohesive forces (existing within the liquid) and the adhesive forces (between the liquid and the solid) (Jaycock & Parfitt, 1981). The situation can be represented by figure 4.2b.

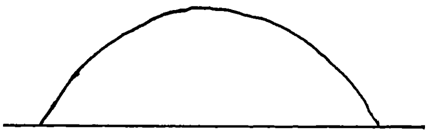

Figure 4.2a Schematic diagram of a liquid drop on a solid surface.

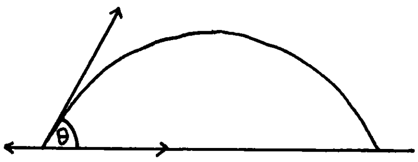

Figure 4.2b Diagram of the forces acting on the liquid in equilibrium on the surface.

The liquid will form an angle, known as the contact angle (Θ), on the solid surface. Now consider the forces involved at the point of contact of the three phases. For an additional unit of solid area to be wetted, there will be a surface free energy increase at the solid-liquid interface (γ_{sl}), a decrease at the solid-vapour interface (γ_{sv}), and an increase at the liquid surface ($\gamma_{lv}\cos\Theta$) (Jaycock & Parfitt, 1981). Resolving the forces involved gives:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad \text{Eqn 4.1.}$$

This equation can be rewritten as:

$$\cos\theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \qquad \text{Eqn 4.2.}$$

Equations 4.1 and 4.2 hold provided $\gamma_{sv} - \gamma_{sl} \leq \gamma_{lv}$ (Schrader & Loeb, 1992).

Theoretically, when $\theta = 0°$ ($\cos\theta = 1$), the liquid spreads spontaneously over the surface and wets the solid completely (Kinloch, 1987). Liquids giving a contact angle less than 90° are also considered to wet the solid surface. For a contact angle of less than 90° to be formed, $0 < \cos\theta \leq 1$. Therefore, it can be deduced from equation 4.2 that

$$\gamma_{sv} - \gamma_{sl} > 0$$

and hence

$$\gamma_{sv} > \gamma_{sl}$$

If $\gamma_{sv} < \gamma_{sl}$, $\cos\theta < 0$, and $\theta > 90°$. In this case, the liquid will not wet the solid, but will remain in a droplet on the surface of the solid.

4.1.ii Critical surface tension.

To predict from the equations above whether a liquid will spread on a solid, it is necessary to know the surface free energies of the phases involved. It is an easy matter to measure the surface free energy of a liquid in equilibrium with its vapour (γ_{lv}), but not to measure the surface free energy of a solid (γ_{SV}), therefore indirect methods have been applied to the situation. To characterize the wettability of low energy solid surfaces, Zisman plots have been used (Berg, 1993). They are evaluated in the following manner. A number of homologous non-wetting liquids with a range of surface tensions are placed on a given surface, and the contact angles evaluated (Plueddemann, 1991). A plot of the cosines of the contact angles versus the surface tensions of the liquids is then constructed (figure 4.3).

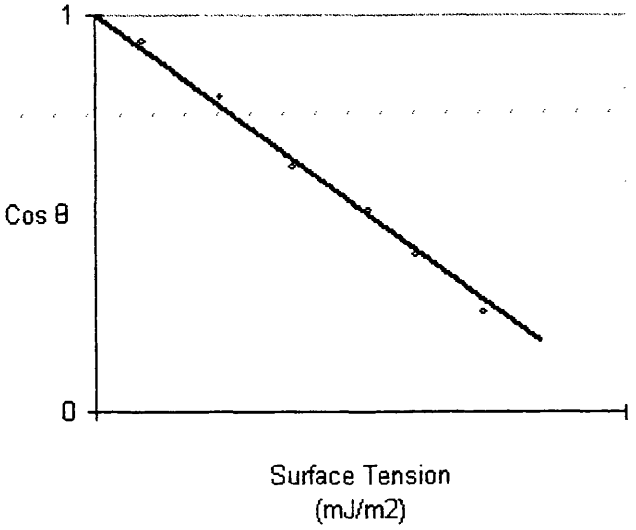

Figure 4.3 A Zisman plot of surface tension v. cos θ for a homologous series of liquids (from Schrader & Loeb, 1992).

The plot is extrapolated to cosθ=1, i.e. θ=0°, which represents the point where a liquid would just spread spontaneously if applied as a drop (Schrader & Loeb, 1992). This point was named by Zisman the critical surface tension (γ_C) of the solid surface (Schrader & Loeb, 1992). The value γ_C is defined as the "limiting surface tension such that a liquid with a surface tension below the critical surface tension of the solid will wet the solid with a zero contact angle" (Good, 1977). It is important to point out that γ_C is not the surface free energy of the solid, but is an empirical parameter closely approximated to γ_{SV} (Schrader & Loeb, 1992). Plueddemann (1991) states that it is without thermodynamic basis: it is the highest surface tension of a liquid that will spread spontaneously on a given surface. Zisman plots have their disadvantages. The critical surface tension is often low compared with surface tensions determined by extrapolation of data from melts or solutions (Schrader & Loeb, 1992). When liquids with polar or hydrogen bonds are used, the Zisman plot tends to be strongly curved and the critical surface tension is difficult to determine (Plueddemann, 1991; Schrader & Loeb, 1992). However, critical surface tension is a useful concept that has been employed to characterize the surface of silanes (Plueddemann, 1991). It will be used in this thesis as an empirical measurement to determine the wettability of some solid surfaces by various liquids.

4.1.iii Factors affecting wetting of solids by liquids.

The surface free energy of a solid is different depending upon the other phase it is in contact with. The surface free energy of a solid in contact with an adsorbed layer of vapour (γ_{SV}) is lower than that of the solid in a vacuum (γ_S) (Kinloch, 1987). Solid mineral surfaces are classed as high energy surfaces. However, many hydrophilic minerals in equilibrium with atmospheric moisture are covered with a layer of water, which will reduce the critical surface tension of the solid (Plueddemann, 1991).

From equation 4.2, it can be seen that a reduction in γ_{Sl} facilitates wetting. Surface roughness can affect the contact angle. If Θ is less than 90° on a smooth plane, Θ will decrease with an increase in surface roughness (Morra et al., 1990). Conversely if Θ is greater than 90° on a smooth plane, the angle will increase with an increase in surface roughness (Morra et al., 1990).

The method of formation of the solid surface is an important factor. Substances that have crystallised in contact with water often produce a lower contact angle with water than if they had crystallised in air, since hydrophilic groups in the solid will be orientated outwards in the former case (Shaw, 1992).

4.2 IMPLICATIONS FOR APPLICATION OF CONSOLIDANT.

For a consolidant to wet and penetrate stone, the liquid must have a surface free energy (γ_{lv}) lower than the critical surface tension of the stone. For salts to hinder the progress of consolidant, they would have to have a critical surface tension lower than the surface free energy of the liquid consolidant. Inorganic materials, such as ceramics and stone, have high energy values, above 500 mJm^{-2} (Wake, 1982). Generally, hydrocarbon polymers have surface free energies of less than 100 mJm^{-2} (Kinloch, 1987). Therefore most organic polymers used as stone consolidants (for example acrylic resins, perfluoropolyethers) should wet stone. Silanes are semi-organic compounds. The surface tension of poly dimethyl siloxane (PDMS) is given as 20.4 mJm^{-2} (Kendrick et al., 1989). This is low because of the low surface energy of the methyl groups. Substituting the methyl groups with other higher alkyl groups increases the surface tension of the polymer (Kendrick et al., 1989). Therefore, the surface tension of methyl trimethoxy silane, with a more polar methoxy group substituting a methyl group, will have a higher surface tension. However, the surface tension will not be higher than the critical surface tension of stone, hence silanes will also wet stone.

The surface free energies of molten salts have been determined experimentally (see for example Reiss & Mayer, 1961; Pandey et al., 1981). These results are usually extrapolated to room temperature to produce an estimated surface free energy for the solid salt. Van Zeggeren & Benson determined the surface free energy of sodium chloride in a saturated ethanol solution to be 171 mJm^{-2} (van Zeggeren & Benson, 1957). As these figures are higher than the surface free energies of the liquid consolidants, the consolidants should wet the salts as they enter the stone. Therefore, viewed from the surface free energies of the situation, the salts should not affect penetration of the consolidant into the stone.

4.3 OTHER POSSIBLE INTERACTIONS.

Pühringer and Weber suggest that as alkyl alkoxy silanes enter the stone, the liquid is able to physically dislodge salts from the surface of the mineral substrate (Pühringer & Weber, 1988). They suggest this occurs because of the silanes' "high spreading power and low surface tension and viscosity". It is possible that they are referring to a situation where the combined interfacial energies between the liquid and stone, and liquid and salt are less than the interfacial energy between the stone and salt. In this situation, it is conceivable that the liquid may dislodge the salts from the surface of the stone, and the salt-stone-silane system will reach a lower energy state.

The salts may also physically hinder penetration of the consolidant. Salts may crystallise across pores and block them, thus reducing the porosity of the stone and preventing access of the consolidant into the blocked pore. A reduction in effective pore size, if not complete blockage of a pore, will also hinder progress of the consolidant through the stone. In experiments, Fritsch and Schamberg (1988) discovered that sodium sulphate inside stone samples reduced the initial uptake of a silane consolidant compared to the uptake of the consolidant by stone samples containing sodium chloride or potasium nitrate. Before treatment, the salt-contaminated stones were stored in 100% RH conditions. Fritsch and Schamberg conclude that in these conditions, the chloride and nitrate salts would have hydrated. However, the the sulphate would not be dissolved, and the salt would block the pore, reducing the pore volume (Fritsch & Schamberg, 1988).

4.4 SUMMARY.

From consideration of the surface energy situation, it is possible to predict that salts will not affect the ability of the consolidant to wet the surface of the stone. However, salt formations in the pores of the stone will hinder penetration of the consolidant.

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5. INTERACTIONS DURING CURING OF THE CONSOLIDANT.

5.1 INTRODUCTION.

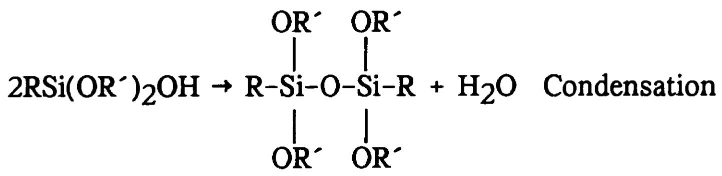
After the consolidant has entered the stone, there may be interaction between salts and consolidant as the consolidant cures. Curing involves polymerisation of the consolidant and/or evaporation of a solvent to leave the solid in situ. For example, Paraloid B72 is applied as a polymer dissolved in a solvent (usually acetone or toluene), and cures by evaporation of the solvent leaving the polymer behind. Epoxy resins are two-part resins, the two components polymerising upon contact with no solvent liberated from the reaction. Methyl trimethoxy silane can be applied as a monomer dissolved in solvent, and polymerises upon contact with water - in this reaction methanol is liberated. The salts and consolidants therefore have the potential to affect each other. Salts may affect polymerisation of the consolidant, and any solvent present may dissolve the salt. The following is a discussion of these possible reactions.

5.2 EFFECTS OF SALTS ON THE POLYMERISATION OF SILANES.

5.2.i Silane chemistry.

Silanes polymerise from the monomer via a two-stage reaction. The two stages are hydrolysis of the monomer to produce a silanol, and condensation of the silanol into a polymer (figure 5.1). However, the process is not a simple linear reaction. Once a silanol has formed, it may be further hydrolysed, or may be subject to condensation. Hence hydrolysis and condensation reactions occur simultaneously after initiation of the reaction sequence. Figure 5.2 shows a cascade of possible reactions occuring during the polymerisation of a trialkoxy silane.

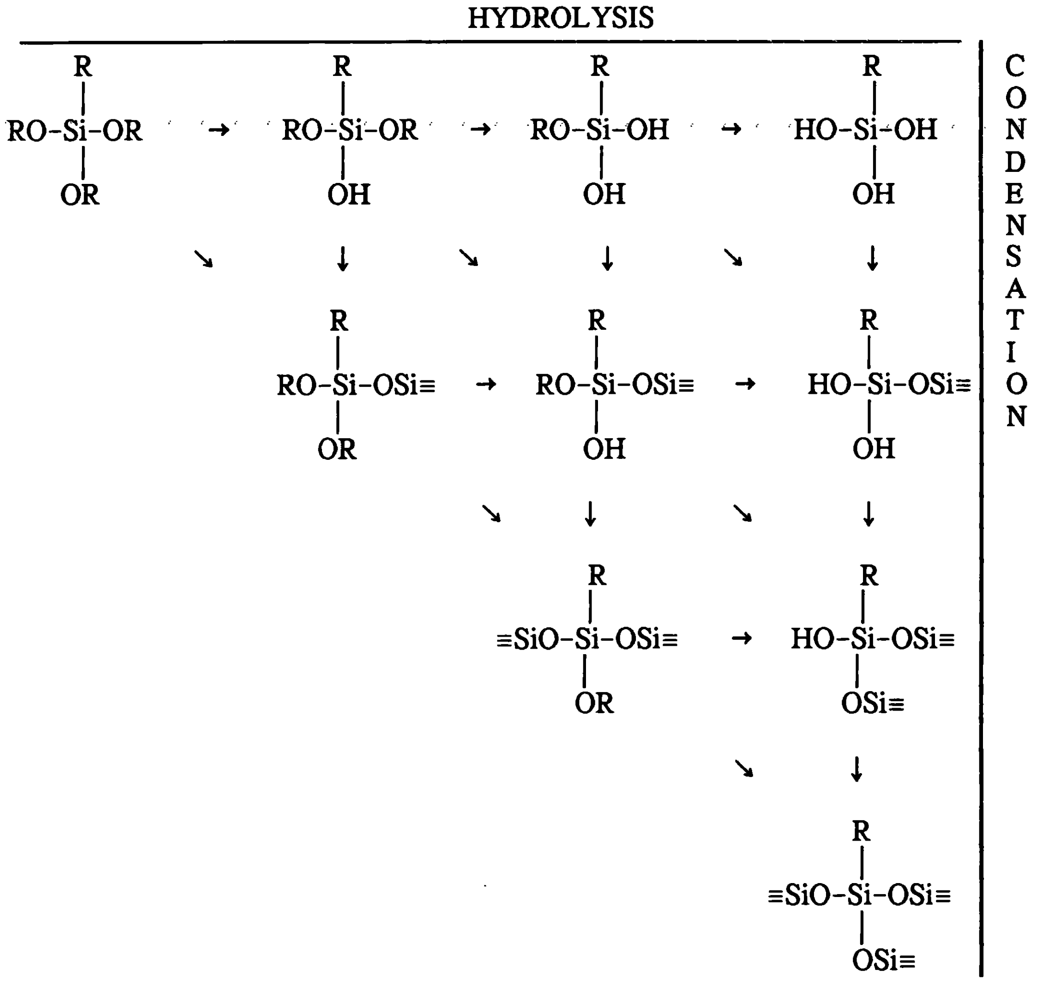
$RSi(OR')_3 + H_2O \rightarrow RSi(OR')_2OH + R'OH$ Hydrolysis



$$2RSi(OR')_2OH \rightarrow R\text{-}\overset{OR'}{\underset{OR'}{Si}}\text{-}O\text{-}\overset{OR'}{\underset{OR'}{Si}}\text{-}R + H_2O$$ Condensation

R, R' = CH_3, C_2H_5, etc.

Figure 5.1 Simplified view of the polymerisation of an alkyl alkoxy silane (from Charola et al., 1984).



R = CH_3, C_2H_5, etc.

Figure 5.2 Alkoxy silane hydrolysis cascade reaction (from Arkles et al., 1992).

5.2.ii Effect of environment on polymerisation of silanes.

The route via which polymerisation proceeds is dependent upon the conditions prevailing both before and at the time of polymerisation. The reaction does not necessarily go to completion, and a number of end-products may be formed. The effects of different parameters on the polymerisation process ha~~s~~ve been studied in detail.

Solvent.

Water is necessary for hydrolysis of the silane. At low relative water contents, reaction is incomplete. Lewin and Wheeler (1985) recommended not relying upon moisture in the stone to provide sufficient water for the reaction. Charola et al. (1984) discovered that at lower RH's the monomer evaporated more than at higher RH's, and the lack of water did not allow the hydrolysis reaction to proceed to completion. Wheeler (1987) found that increasing the percentage of water in a system containing tetra ethoxy silane, water and ethanol produced more silanols. If gelation could occur at a ratio of less than 1.5 parts of water to 1 part of silane, the hydrolysis of the silanol was faster than hydrolysis of the monomer; if gelation did not occur, then hydrolysis was slower for the silanol than for the monomer (Wheeler, 1987).

Wheeler also discovered that other solvents used play a significant role in the kinetics of hydrolysis. For example, ethanol appeared to hamper the hydrolysis reaction (Wheeler, 1987).

Substituted organic groups.

The size of the alkoxy group affects the rate of polymerisation. For example, a methoxy silane hydrolyzes at 6 to 10 times the rate of an ethoxy silane (Arkles et al., 1992). The rate is also affected by the degree of organic substitution of the alkoxy groups (Arkles et al., 1992). Wheeler (1987) found that hydrolysis and condensation reactions of methyl triethoxy silane were faster than tetra ethoxy silane. Wheeler attributed this to greater access being provided to the silicon atom by the substitution of an ethoxy by a methyl group (Wheeler, 1987).

pH.

pH has a marked effect on both the hydrolysis and condensation reactions. The rate of acid hydrolysis is significantly greater than base hydrolysis (Arkles et al., 1992).

The final form of the polymer is influenced by the pH. Polymerisation occurs in three stages:
a. polymerisation of monomer to form particles;
b. growth of particles;
c. linking of particles together into branched chains, then networks, and finally extending through the liquid, thickening it to a gel (Iler, 1979).

In basic solutions, particles in solution grow in size and diminish in number as smaller particles dissolve and silica is redeposited on the larger particles (Iler, 1979). This effect is known as Ostwald ripening. At pH's greater than 6 or 7, the particles are negatively charged and repel each other, therefore they don't collide. No gel is formed, only gel particles.

In acidic conditions, the silica particles bear little ionic charge, and hence collide and aggregate into chains (Iler, 1979). The particle size is much smaller, the particles aggregating to form a three-dimensional network. This leads to a highly crosslinked gel (Wheeler, 1987). The situation is represented in figure 5.3.

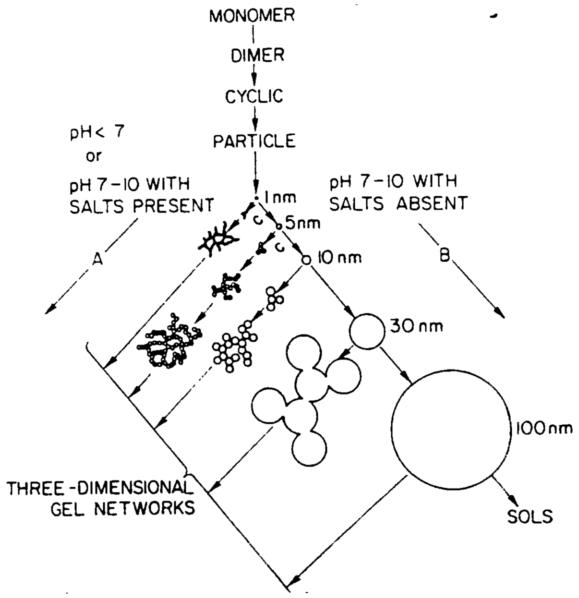


Figure 5.3 Effect of pH on polymer formation (from Iler, 1979).

Goins (1994) discovered that both sandstones and limestones have acidic surfaces in non-aqueous, non-polar solvents. The pH of a sandstone-tetra ethoxy silane-water-ethanol system was approximately 5 to 6. In the presence of limestone or marble rather than sandstone, the pH rose to approximately 7 to 8, or more. This would suggest that a network polymer would form in sandstones. Indeed, Chiari observed the formation of small particulate networks in adobe treated with silanes. In different studies, Mavrov (1983) and Chiari (1987) charted the polymerisation of silanes. Chiari looked at a partially polymerised ethyl silicate (Silester ZNS) applied to adobe. Mavrov studied 3 different silane-based resins (Wacker OH, Rhone-Poulenc X54-802 and Drisil 773) which were deposited on glass plates or nickel plates to allow their study by transmission electron microscopy (TEM). Chiari observed that one day after treatment, smaller pores in the adobe were covered with the resin. After 7 days the coating had transformed into a network of filaments which broke by contraction. Large blocks of gel evolved into empty round vesicles. Chiari states that his observations confirm "the slowness of the hydrolysis reaction" (Chiari, 1987). Mavrov observed a similar pattern of initial amorphous film formation followed by contraction of the film and the formation of individual threads which connected, forming a spatial net-like structure.

Salts.

There have been very few studies into how salts affect the polymerisation of silanes. Clayden & Jones (1993) discovered that there was a strong interaction between magnesium chloride and alkyl alkoxy silanes before polymerisation started. They hypothesised that there was a small increase in the partial positive charge on the silicon, and a change in the geometry around the silicon to maximize the co-ordination to the surface of the magnesium chloride (Clayden & Jones, 1993).

Kumar and Price (1994) examined the effects of several different salts on the hydrolysis and condensation of methyl trimethoxy silane. Their results confirm the fact that individual salts react in different ways and produce different results, precluding any generalization of the situation. Sodium sulphate and magnesium sulphate radically retarded the rate of hydrolysis from 10 minutes to 30-50 minutes, whilst sodium chloride, magnesium chloride and sodium nitrate slowed down hydrolysis by only a few minutes. Sodium sulphate and magnesium sulphate also delayed the time to phase separation by a significant amount. In contrast, sodium chloride, sodium nitrate and magnesium chloride increased the rate of phase separation. Kumar suggests that the different reactions may be due to the pH of the salts, with the more acidic salts increasing the rate of condensation. Iler (1979) states that salts lower the ionic charge on the particles formed by the silane, leading to the formation of a network, even in an alkaline environment (see figure 5.3).

Danehey et al. (1992) looked at the influence of quartz and calcite on the polymerisation of methyl trimethoxy silane. They discovered that quartz had little effect on the rates of hydrolysis and condensation, but calcite retarded the condensation reactions. Further experiments revealed that it was not dissolved calcite, but solid calcite crystals that retard the condensation process (Danehey et al., 1992).

Kumar and Price (1994) suggest that the delay in hydrolysis could allow large quantities of the monomer to evaporate before polymerisation. Danehey et al. (1992) suggest that slowing down the condensation rate allows evaporation of the silane before having the opportunity to function as a consolidant. Therefore, it would appear that fast reaction rates are advantageous for silane consolidation. However, Pühringer and Weber (1990) state that slow hydrolysis rates of alkyl alkoxy silanes seem to increase their ability to extract salts from stone. This may arise from the fact that slow hydrolysis allows large quantities of the silane to evaporate before gelling, leaving porosity of the stone virtually unchanged and not restricting the flow of salt solutions through the stone.

5.3 SOLUBILITY OF SALTS IN CONSOLOIDANTS.

One possibility is that salts may dissolve in any solvent present, or in the liquid monomer or polymer. The extent to which a solid is soluble in a liquid is difficult to predict, but the type of liquid that a solid is most likely to dissolve in may be anticipated using the principle of 'like dissolves like', that is a solid will dissolve in a liquid having similar properties (James, 1986). Solvation depends upon the relative values of the intermolecular pair potential energies of the solid and liquid. If the affinity of a solvent's particles for other solvent particles is greater than their affinity for a solute particle, the solute will be excluded from the solvent and will not dissolve. Similarly, if the attraction between solute particles is greater than that between solute and solvent, the solvent will not dissolve the solute. For dissolution of the solute, mutual attraction between the solvent and the solute must be greater than or equal to the attractive forces between the solvent particles and the forces between the solute particles. James (1986) suggests the following classification system to determine the solubility of a solid in a liquid.

1. Electrolytes dissolve in conducting solvents.
2. Solutes containing hydrogen capable of forming hydrogen bonds dissolve in solvents capable of accepting hydrogen bonds, and vice versa.
3. Solutes with significant dipole moments dissolve in solvents having significant dipole moments.
4. Solutes with low or zero dipole moments dissolve in solvents with low or zero dipole moments.

The solubility of a solid in a liquid can be only partially estimated using the above principles. Melting point and enthalpy of fusion of the solute need to be considered when discussing systems with identical interparticulate forces (Reid et al., 1977). Increasing molecular weight increases the complexity of the situation, involving combinations of groups with differing hydrophilic and hydrophobic properties (James, 1986). Solubility is also affected by other dissolved species (for example salts), pH, and temperature (James, 1992). Also, there are certain combinations of solutes and solvents that prove exceptions to the general rules (James, 1986).

5.3.i The solubility parameter.

The solubility parameter is a term used to describe the capacity of a liquid to dissolve another material. The solubility parameter (δ) is related to the cohesive energy density (CED) of a liquid, and is defined as:

$$\mathrm{CED} = \delta^2 \qquad \text{Equation 5.1}$$

The cohesive energy density is a direct measure of the total molecular cohesion per cubic centimetre of liquid (Lee, 1970). For hydrogen-bonded liquids, the CED was found to be high, because a large part of the cohesive energy is created by the hydrogen bonding. The CED of a liquid also affects surface tensions (Lee, 1970). A liquid with a high CED invariably yields a high surface tension.

The basis of the solubility parameter concept to mixtures is described by Barton (1983) as follows. A material with a high solubility parameter requires more energy for dispersal than is gained by mixing it with a material of low solubility parameter, so immiscibility results. Two materials with similar solubility parameter values gain sufficient energy on mutual dispersion to permit mixing.

However, it was found that some solvents with the same solubility parameter had very different solvation properties for the same material (Hedley, 1980). This is because there are different types of internal forces acting between molecules, each of which contribute to varying degrees to the cohesive energy density, and thus the solubility parameter. Two liquids may have the same solubility parameter value, but different types of intermolecular forces acting to produce that value, hence the liquids will have differing solvation properties. The three main categories of intermolecular forces, namely dispersion, polar and hydrogen bonding forces, were used to subdivide the solubility parameter into terms that would more usefully describe the characteristics of solvents (Hedley, 1980). Hence equation 5.1 is expanded to:

$$\mathrm{CED} = \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad \text{Equation 5.2}$$

where δ_d = parameter due to dispersion forces
δ_p = parameter due to polar forces
δ_h = parameter due to hydrogen bonding

The partial solubility parameters δ_d, δ_p and δ_h are known as Hansen parameters, named after the person who proposed equation 5.2 (Hansen, 1967).

A method of displaying the information about partial solubility parameters in an easily understandable format was proposed by Teas (1968). He proposed using a two-dimensional triangular graph. The three axes on the graph, f_D, f_P, and f_H are based upon the Hansen parameters, and are defined as:

$$f_D = \frac{100\delta d}{\delta_d+\delta_p+\delta_h} \qquad f_P = \frac{100\delta p}{\delta_d+\delta_p+\delta_h} \qquad f_H = \frac{100\delta h}{\delta_d+\delta_p+\delta_h} \qquad \text{Equation 5.3}$$

An example of a Teas chart can be seen in figure 5.4. This chart shows at a glance the location of different types of solvents. Solvents that are close to each other in the chart have similar solvent powers. Therefore, the chart can be used to determine logically which solvents a solid may be soluble in, if the solid's solubility is known in other solvents.

5.3.ii Solubility of salts in some commonly used solvents.

The solubility of salts in solvents commonly used in conservation is documented in chemistry textbooks. Table 5.1 lists the solubility of some salts in solvents which may be present during the consolidation process.

As can be seen from table 5.1, the solubility of the salts decreases as the polarity of the solvent decreases. Their solubility in water decreases as the proportion of less polar solvent increases. For example, a saturated solution of sodium sulphate decahydrate in a mixture of 19.88 wt% ethanol in water (at 25°C) will contain 6.00 wt% of the salt (Stephen & Stephen, 1963). As the weight percentage of ethanol increases in the solution, the solubililty of the salt

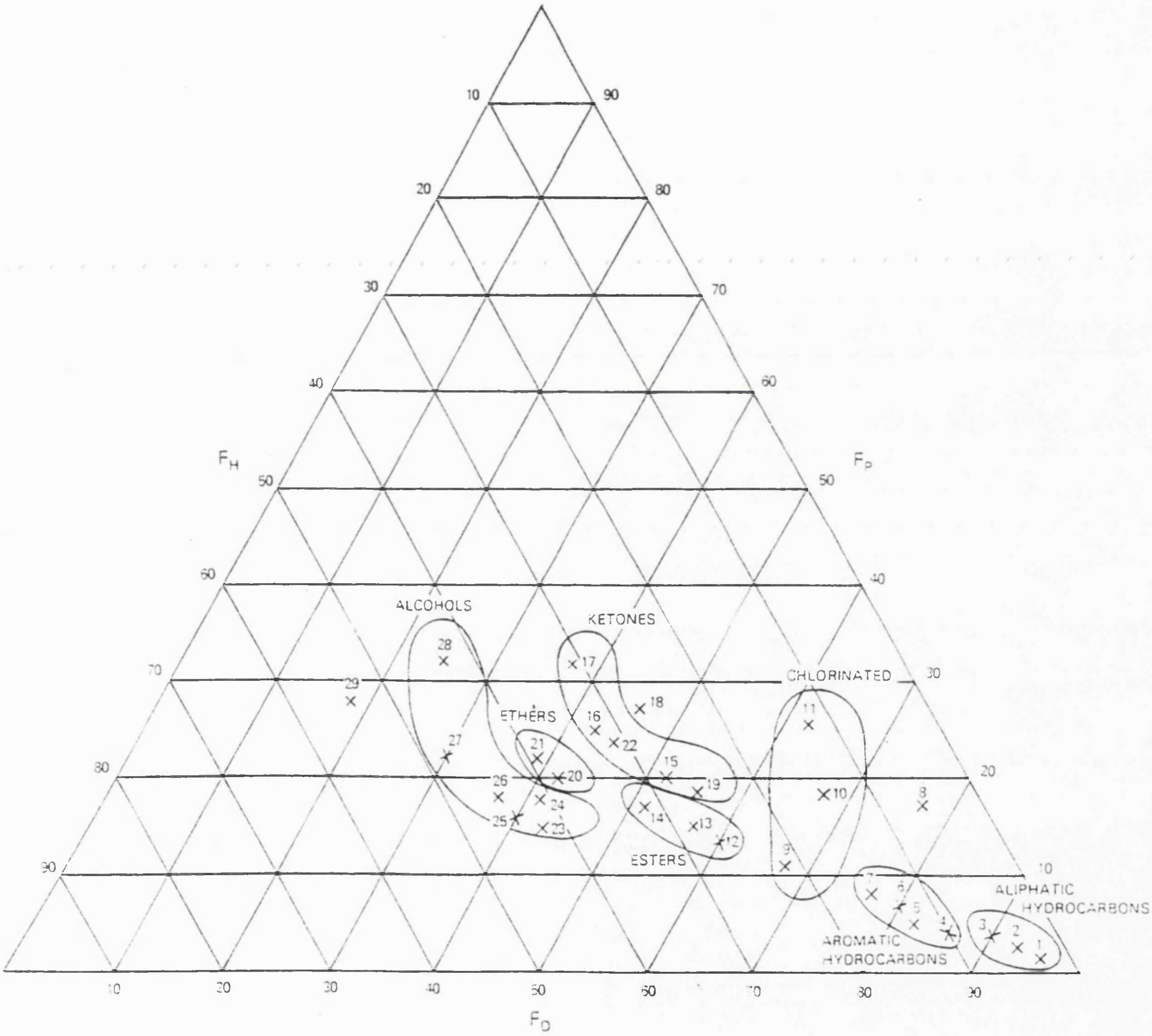


Figure 5.4a The Teas chart showing individual solvents and the approximate location of family groups (from Hedley, 1980).

No.	Solvent	Teas Fractional Solubility Parameters		
		f_D	f_P	f_H
1.	Hexane (n-hexane)	96	2	2*
2.	VM & P Naphtha	94	3	3
3.	White Spirit	90	4	6
4.	Ethyl benzene	87	3	10
5.	Xylene (dimethylbenzene)	83	5	12
6.	Toluene (methylbenzene)	80	7	13
7.	Benzene	78	8	14
8.	Turpentine	77	18	5
9.	Chloroform (trichloromethane)	67	11	22*
10.	Ethylene chloride (1,2-dichloroethane)	67	19	14
11.	Methylene chloride (dichloromethane)	62	26	12
12.	Butyl acetate	60	13	27
13.	Propyl acetate	57	15	28
14.	Ethyl acetate	51	18	31
15.	Methyl isoamyl ketone (5-methyl-2-hexanone)	62	20	18
16.	Methy ethyl ketone (2-butanone)	53	26	21
17.	Acetone (2-propanone)	47	32	21
18.	Cyclohexanone	55	28	17
19.	Tetrahydrofuran	55	19	26
20.	Ethyl Cellosalve (2-ethoxyethanol)	42	20	38
21.	Methyl Cellosalve (2-methoxyethanol)	39	22	39
22.	Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)	45	24	31
23.	n-Butyl alcohol (1-butanol)	43	15	42
24.	iso-Propyl alcohol (2-propanol)	41	18	41 +
25.	n-Propyl alcohol (1-propanol)	40	16	44
26.	Ethyl alcohol (ethanol)	36	18	46
27.	Methyl alcohol (methanol)	30	22	48
28.	Glycerol (1, 2, 3-propantriol)	25	23	52
29.	Water	18	28	54

Parameters are as quoted by Torraca[6] from "Predicting Resin Solubilities" by J. P. Teas, printed by Ashland Chemicals Co., Columbus, Ohio.

* Parameters taken from Teas, "Graphic Analysis of Resin Solubilities"[12].

\+ Parameter calculated directly from Hansen parameters quoted in Shell Technical Bulletin ICS/78/1[11].

This list is entirely for comparative purposes and many of the chemicals are not recommended for use by conservators[23].

Figure 5.4b The Teas fractional solubility parameters (from Hedley, 1980).

decreases. At 79.67 wt% ethanol, the solution will dissolve only 0.002 wt% of the salt (Stephen & Stephen, 1963). It is possibly this decrease in solubility that Pühringer and Weber are referring to in their article on salt extraction principles (1990). They discuss the ability of solvents that do not dissolve salts (for example alcohols) to act as "indirectly extraction-active preparations... (that) ...change the salt concentration by extracting water from salt solution". It appears that they are describing the reduction in solubility of salts and their precipitation from solution when an alcohol is added to a water-salt solution.

	Sodium chloride	Sodium nitrate	Sodium sulphate decahydrate
Water	35.83[1]	46.7-46.8[1]	28.0[1]
Methanol	1.401[2]	0.41[2]	0.056[1]
Ethanol	0.0649[2]	0.036[2]	0.01[1]
Acetone	4.05×10^{-5}[3]	1.98[4]	

[1] =g per 100g solvent at 20°C

[2] =g per 100g solvent at 25°C

[3] =g per 100g solvent at 18°C

[4] =g per solution of 90g acetone + 10g water at 30°C

Table 5.1 Solubilities of some salts in solvents (from Linke, 1965; Stephen & Stephen, 1963).

In alcohols, the solubility of sodium chloride decreases as the molecular chain length increases. At 25°C, 1.401g of sodium chloride will dissolve in 100g methanol, decreasing to 0.0124g in 100g propan-1-ol (Linke, 1965). The solubility of salts increases as temperature increases. For example, the solubility of sodiun chloride in acetone rises from 3.2×10^{-5}g per 100ml saturated solution at 18°C to 3.5×10^{-5}g per 100ml saturated solution at 37°C (Linke, 1965).

5.3.iii Solubility of salts in silanes.

The solubility parameter, and partial solubility parameters, can be used to determine the solubility of salts in silanes. Allen (1992) lists the solubility parameters of some liquids, with their hydrogen-bonding character (see table 5.2).

Liquid	Solubility parameter (mJm^{-3})	Hydrogen bonding character
Toluene	18.2	Poor
Acetone	20.4	Moderate
Ethanol	26.1	Strong
Methanol	29.6	Strong
Water	47.9	Strong

Table 5.2 Solubility parameters of liquids
(from Allen, 1992).

Plueddemann (1968) gives the solubility parameter of poly dimethyl siloxane as 7.3 and an ethyl triethoxoxy silane as 7.0. These figures are much lower than the solubility parameters of water and alcohols, in which salts are most soluble. This suggests that salts will not be soluble in silanes.

From a comparison of tables 5.1 and 5.2, and figure 5.4, it can be seen that salts soluble in water become increasingly more insoluble in solvents to the right of water in the Teas chart, that is as the hydrogen bonding fractional parameter decreases. Plueddemann (1991) gives the Hansen parameters for methyl trimethoxy silane and propyl trimethoxy silane. When converted to partial parameters using equation 5.3, $f_D = 100$, $f_P = 0$, $f_H = 0$ for both silanes. This places them in the far right hand corner of the Teas chart, far outside the region of solubility of salts. This substantiates the earlier conclusions about the insolubility of salts in unpolymerised silanes.

As the silanes hydrolyse, the hydrogen bonding parameter will increase with the proportion of silanol in the solution. Also, alcohol can be released from the hydrolysis reaction of silanes. However, salts are only sparingly soluble in alcohols, and hence the salts may at most be sparingly soluble in the silane and the products of polymerisation..

5.4 SUMMARY.

During curing of the consolidant, there is the possibility of interaction with salts in various ways. Salts are only sparingly soluble in alcohols and ketones. However, some are soluble in water, to varying degrees. When a consolidant containing water (such as a silane-alcohol-water solution) enters the stone, dissolution of a soluble salt will lead to its redistribution as the consolidant moves around the stone.

There is strong evidence that salts affect the polymerisation of silanes. Salts influence both the hydrolysis and condensation reactions, but to varying extents, and with different results. Polymerisation may be slowed enough to allow significant amounts of the consolidant to evaporate, thus reducing the effect of consolidation. The final polymer structure will also be affected.

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6. RELATIONSHIPS AFTER CONSOLIDATION.

6.1 INTRODUCTION.

After consolidation of salt-laden stone, there may be interaction between the salts and consolidant if water or water vapour is able to reach and activate the salts. Most authors examine the situation between salts and consolidants immediately after curing. A further consideration is the situation when fresh salts enter consolidated stone, an event that will often occur on buildings or objects subject to salt formation processes. In this chapter, the observations of other authors, and possible reasons for their observations will be discussed.

6.2 OBSERVATIONS OF SALT ACTIVITY AFTER CONSOLIDATION.

Conservators have noticed that salts have still been active after consolidation. At the Victoria and Albert Museum, London, a limestone statue was consolidated with methyl trimethoxy silane (Larson, 1980). Three days after treatment, the statue was covered in tiny droplets of water, which were found to contain chloride and nitrate ions. Similar experiences were reported on treated objects at the British Museum. Limestone objects were consolidated with an acrylic silane, Raccanello, and left to cure for 6 weeks (Bradley & Hanna, 1986). In the following three months, droplets of moisture appeared on the surface. Another limestone object treated with Raccanello was found to be covered in a heavy efflorescence two years after treatment (Bradley & Hanna, 1986). Analysis of the droplets of water revealed the presence of chlorides and nitrates.

Larson (1980) concluded that the salts were not encapsulated by the consolidant, and were still absorbing moisture from the atmosphere. He further suggested that the silane had reduced the porosity of the stone and made it hydrophobic, thus moisture was remaining on the surface rather than being absorbed into the stone

(Larson, 1980). Fritsch and Schamberg (1988) discovered that the effective water repellency of the silane they tested was lower when salts were present in the treated stone than when salts were absent. Also, Mavrov (1983) reported that the contact angle (Θ) on the surface of salt-laden, silane-treated stone samples was 22 to 48% lower in comparison with non-salted impregnated samples.

Bradley and Hanna (1986) surmised that the mobility of salts and their movement from within the stone to the surface appeared to be greatly enhanced following treatment with a silane. Larson's postulation (1980) that moisture was remaining on the surface of the stone suggests that the salt ions found in the water droplets were already on the surface of the stone. To discover whether the salts had moved from inside the stone, or were already on the surface, it would be necessary to know where the salts were originally, and track their progress following consolidation.

Some authors have researched the removal of salts from consolidated stone. Theoretically, the consolidant reduces the open pore volume thereby reducing the rate of water passage and subsequently the rate of desalination (Paterakis, 1993). Biscontin and co-workers (1988) saturated stone samples with saline solutions (magnesium sulphate heptahydrate, and sodium chloride), and consolidated the salt-laden stones with methyl phenyl siloxane. The samples were then totally immersed in deionised water baths, and the conductivity of the water measured. Contrary to their expectations, they noticed an immediate salt release at a fast rate. The salt was released from the stone in spite of the presence of the consolidant. Paterakis (1992, 1993) conducted similar tests, but on fired earthenware and calcareous clay tiles. The tiles were impregnated with various salt solutions (calcium acetate, sodium sulphate or sodium chloride) before being consolidated with tetra ethoxy silane, methyl triethoxy silane, or Paraloid B72 (10% w/v in acetone). The two silane-based treatments were introduced to the samples under vacuum impregnation, whilst the Paraloid B72 in acetone was introduced through the base of tiles by capillary absorption (Paterakis, 1992, 1993). The samples were then immersed in deionised water baths, and the conductivity of the water monitored. The tests were repeated but with the water in the baths being constantly stirred, to discover if this increased the rate of salt extraction. With calcium acetate as the salt, she unexpectedly discovered that when the water was not stirred in the baths containing the calcareous ceramic, salt from the unconsolidated tiles was released more slowly than salt from the consolidated tiles (1993). When the water was stirred, the salt was released more quickly from the unconsolidated tiles than from the consolidated tiles (1993). With the earthenware ceramic, again the unconsolidated tiles were not the fastest to release salts. With sodium sulphate as the salt, the salt was released fastest from the samples treated with Paraloid B72, with the slowest salt release from those treated with methyl triethoxy silane (1992). Similar results to this were produced by samples impregnated with sodium chloride (1992).

Mavrov (1983) impregnated stone samples with sodium sulphate, and consolidated them with various silicone and silane treatments. The samples were then subjected to cycles of immersion in sodium sulphate solutions and drying. The destruction of the samples was followed using scanning electron microscopy. Mavrov observed the liberation of salts blocked by the polymer. Pockets of salt that had been covered by resin were broken due to an increase in volume of salts upon moistening. Mavrov states that the hygroscopic nature of unblocked salts permitted penetration of water into internal parts of the stone. After the salts were liberated from the polymer, they migrated towards the stone surface. This caused closing of the pore holes, and forced crystallisation in internal parts of the stone. It is difficult to know whether the salts Mavrov saw had moved from the interior of the stone, since more salts were being introduced into the stone with every salt immersion cycle. It is possible that he observed the crystallisation of newly introduced salts blocking the pores.

6.3 THEORETICAL CONSIDERATIONS.

Once the consolidant has cured inside the stone, salt activation will be prevented if the consolidant can prevent access of water or water vapour to the salt. The observations above demonstrate that salt activity is not being prevented by consolidation. Mavrov (1983) and Chiari (1987) observed the formation of holes during silane film formation, which allow access of water and water vapour to the salts. Once the salts have been activated, they will move in solution, and be redeposited elsewhere in the stone.

To consider where the salts will be deposited requires a discussion about the surface free energies of the solid/air and solid/liquid interfaces.

Solid surface	γ_C (mJm^{-2})
Methyl trimethoxy silane	22.5
Ethyl trimethoxy silane	27.0
Poly methyl methacrylate	39.0
Glass, soda-lime (dry)	47.0
Silica, fused	78.0

Table 6.1 Critical surface tensions (γ_C) of some solids (from Plueddemann, 1970; 1991).

For a liquid to wet a solid, it must have a surface tension lower than the critical surface tension of the solid. Water has a surface tension of 72.8 mJm^{-2} at 20°C (Lee, 1970). As can be seen from table 6.1, this is considerably higher than the critical surface tensions of many polymer surfaces. For dilute salt solutions, it may be assumed that the dissolved salt will not significantly affect the surface tension of the water. For more saturated solutions, the surface free energy will be raised above that of pure water.

To explain the findings of Paterakis (1992, 1993), the possibility of the physical movement of salts during initial application of consolidant must be considered. This movement was suggested by Pühringer and Weber (1990) (see 4.3, page 52). During vacuum impregnation, liquid consolidant would carry the salts further into the stone (figure 6.1a), whereas capillary absorption of a liquid would carry salts towards the upper surface of the sample being treated (figure 6.1b).

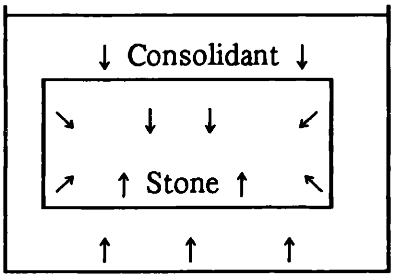


Figure 6.1a Movement of consolidant under vacuum - salts may be transported further into stone.

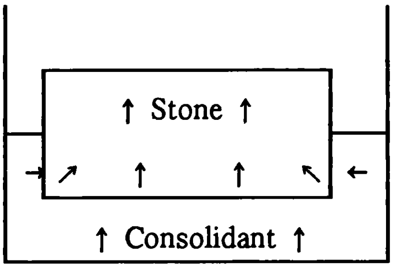
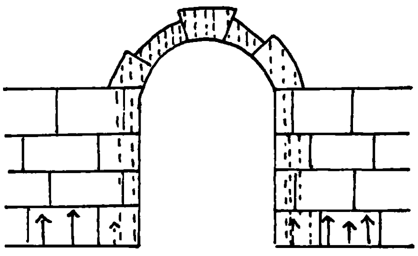


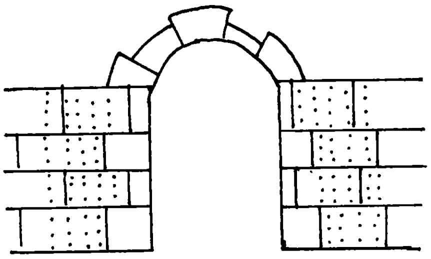
Figure 6.1b Movement of consolidant by capillary absorption through stone, drawing salts to upper surface.

When the samples are placed in water, the salts concentrated at the surface will dissolve before salts positioned further inside the samples. In the experiments of Paterakis (1992, 1993), salt from the samples treated with Paraloid B72 would be released sooner than those from the samples treated with the silanes by vacuum impregnation.

One interesting question that does not appear to have been considered is where do the salts precipitate after consolidation? Will they precipitate preferentially on consolidated or unconsolidated areas in the stone? The question may be answered by considering the surface free energies in the situation. Take as an example a salt-contaminated limestone treated with Paraloid B72 in acetone. The solid

B72 surface has a lower surface free energy (γ_{SV}) than the stone, and a lower critical surface tension (γ_C) than the salt solution. Therefore the salt solution will have difficulty wetting the consolidated surface, and will travel preferentially through unconsolidated pores. The salts will therefore crystallise in these areas rather than in consolidated areas. This is of great importance in situations where salts are a continuing problem. Now consider a limestone porch (figure 6.2a) which has been desalinated and consolidated. If it is subject to further salt influx, the salt solution will travel preferentially through unconsolidated areas, and a salt problem will arise in those areas Figure 6.2b).





⁝ Consolidated stone ⁝⁝ Salt crystallisation

Figure 6.2a Salt movement in solution through a building.

Figure 6.2b Preferential crystallisation of salts in unconsolidated areas.

A further situation to examine is that of the desalination of consolidated stone. Desalination involves the introduction of water into the stone to dissolve the salts. From the above discussion, it can be deduced that the water will travel along unconsolidated or lightly consolidated pores rather than areas of intense consolidation. Salts will be extracted from these areas, leaving salts in consolidated areas untouched. The desalination procedure, therefore, will not be completely effective.

6.4 SUMMARY.

After consolidation, salt movement has still been observed by conservators and researchers. Indeed, in some instances consolidation may have increased salt movement. Clearly this is an area requiring further investigation. The recrystallisation of salts is affected by the presence of a consolidant. The consolidant creates a low energy solid surface on which a salt solution will not spread. Salts crystallise preferentially on a higher energy stone surface. With repeated weathering cycles, salt decay will be concentrated on unconsolidated areas. This is a hazard that must be considered when consolidating areas that will be subject to further salt infiltration.

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7. EXPERIMENTS.

7.1 INTRODUCTION.

From the preceding chapters, questions have been raised about the ability of consolidants to encapsulate salts and prevent further activity of the salts after consolidation. It was decided to investigate these areas of uncertainty through experimentation. The following chapter documents the experiments conducted, and the results from the experiments.

7.2 ENCAPSULATION OF SALTS BY CONSOLIDANTS.

7.2.i Initial Experiments.

The first set of experiments were designed to discover whether a consolidant was capable of forming a coherent layer able to physically encapsulate a range of salts. To simplify the situation, the experiments were conducted on salt crystals alone, and not salts in stone.

Experiment design.

The consolidants tested were:

- Paraloid B72 (20% w/v in toluene);
- Wacker OH - a one component product based upon silicic acid ethyl ester (Wacker product information);
- Wacker H - a one component product containing a silicone to impart water repellency, and ethyl silicate to strengthen the masonry material (Wacker product information leaflet);
- methyl trimethoxy silane (MTMOS) (supplied as Dow Corning Z-6070).

Wheeler reported that the Wacker products are based on tetraethoxy silane, methyl trimethoxy silane, acetone, methylethylketone and dibutyltindilaurate (Wheeler et al., 1991). Bradley agrees that Wacker OH contains tetraethoxy silane, but reports that Wacker H contains ethyl triethoxy silane (Bradley, 1987).

The soluble salts chosen as representative of those found in decayed stone were sodium chloride ($NaCl$), sodium nitrate ($NaNO_3$), sodium sulphate (Na_2SO_4), anhydrous calcium sulphate ($CaSO_4$) and calcium sulphate dihydrate ($CaSO_4.2H_2O$). The tests were also performed on calcium carbonate ($CaCO_3$), as it is the main constituent of calcitic rocks. Standard laboratory grade salts were used in the experiments.

To a small amount of salt (0.1g) on a microscope slide enough consolidant was applied using a pipette to completely cover the salt. This was repeated for every salt and consolidant combination. To check reproducibility of the results, three sets of slides were created for each combination. The prepared slides were left in ambient conditions to allow the consolidant to cure. At each stage of the experiment, the samples were examined using optical and scanning electron microscopy. All scanning electron microscope (~~sem~~SEM) work was performed at 20kv. u.c.

Different humidity environments were created by placing the samples in sealed chambers containing a suitable saturated salt solution. An ambient environment was created using a saturated solution of magnesium nitrate, which produces a relative humidity (RH) of 53% at 20°C. For damp conditions, a saturated solution of potassium chloride was used, which gives an RH of 85% at 20°C. All chambers were stored in the laboratory, where the temperature varied between approximately 18 and 22°C.

Results.

The initial application of consolidant to the salts was observed under an optical microscope. When a drop of consolidant came into contact with a salt, the smaller salt particles moved around with the flow of the liquid. This movement of the salts generated by the introduction of a consolidant appears to corroborate Pühringer and Weber's ideas (1990) that silanes physically dislodge salts as they enter into the stone (see 4.3, page 52).

This movement of salts by consolidants may explain the unexpected observations of Paterakis (1993) described in chapter 6 (page 76). When the tiles were consolidated, the salts may have been carried to the surface of the tiles, a phenomenon that the salts in the unconsolidated tiles would not have been subjected to. Once in a water bath the salts in the consolidated tiles, now concentrated at the surface, would immediately be dissolved in the water, whereas salt in the unconsolidated tiles would require more time for water flow into the tiles.

Table 7.1 summarizes the ability of the various consolidants to form a film or covering on the salts after curing in ambient environmental conditions.

As can be seen from figures 7.1 and 7.2, Wacker H and Wacker OH formed thin, cracked films on the surface of the different salts. The films had cracked both in areas between salt crystals and over the surface of the crystals. Interestingly, flawless films had formed in areas where no salts were present (see figure 7.3). When handled, the Wacker OH film was more brittle than the Wacker H sample. Indeed, the Wacker OH failed to keep the salts on the slide when handled (see figure 7.3).

	NaCl	$NaNO_3$	Na_2SO_4	$CaCO_3$	$CaSO_4$	$CaSO_4 \cdot 2H_2O$
Wacker H	Cracked film	Cracked film	Cracked film	Cracked film	Cracked film	Cracked film
Wacker OH	Cracked film	Cracked film	Cracked film	Cracked film	Cracked film	Cracked film
Z-6070	No film visible	No film visible	No film visible	No film visible	No film visible	No film visible
Paraloid B72	Intact covering	Intact covering	Intact covering	Intact covering	Intact covering	Intact covering

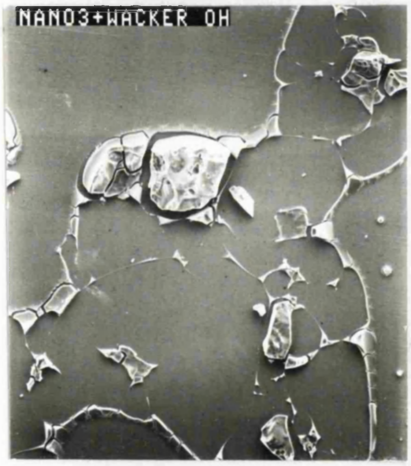
Table 7.1 Type of film formed on salts after curing.

Figure 7.1 SEM ~~sem~~ photograph of sodium chloride and Wacker OH, revealing cracks in the polymer film.

100µ

Figure 7.2 ~~sem~~ SEM photograph of sodium nitrate and Wacker H. Cracks in the polymer film can be seen.

uc



0.6mm

Figure 7.3 ~~sem~~ SEM photograph of sodium nitrate and Wacker OH. Salts have become detached from the surface of the slide despite consolidation. In areas where no salts were originally present (top left and bottom right), a flawless film has formed.

uc

When examining the salts treated with MTMOS, no film could be seen on the salts (figure 7.4). It appeared that the silane had evaporated before polymerisation. Analysis of the surface by energy dispersive X-ray (EDAX) of a treated sodium chloride crystal revealed a very small amount of Si present, which was sparsely distributed over the crystal surface (figures 7.5, 7.6, 7.7).

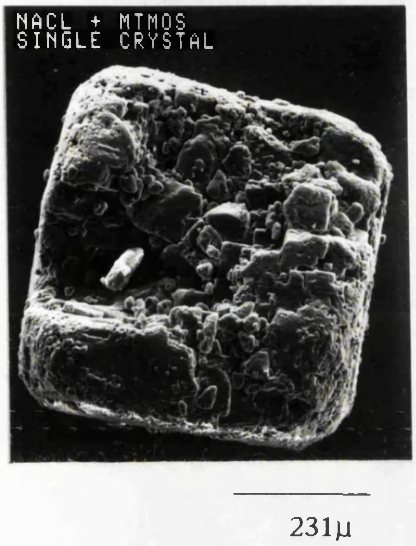


Figure 7.4 ~~sem~~ SEM photograph of sodium chloride and MTMOS.

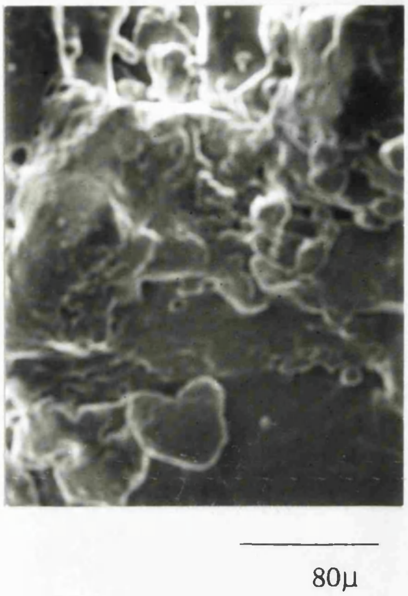


Figure 7.5 Surface analysed by EDAX.

Figure 7.6 Dot map of Cl. Light areas indicate presence of Cl.

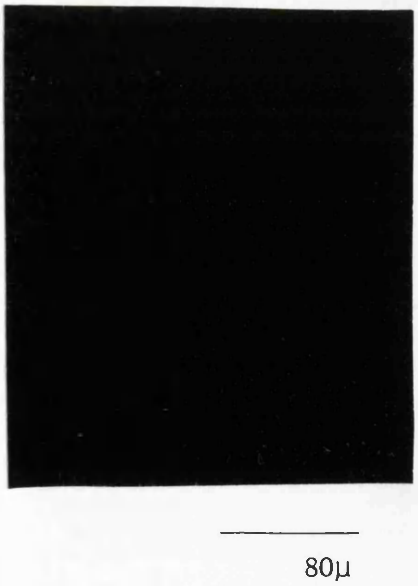


Figure 7.7 Dot map of Si. Light areas indicate presence of Si.

The only consolidant tested that created a continuous layer over the salts was Paraloid B72 (figure 7.8). The film formed had no flaws, and was not cracked.

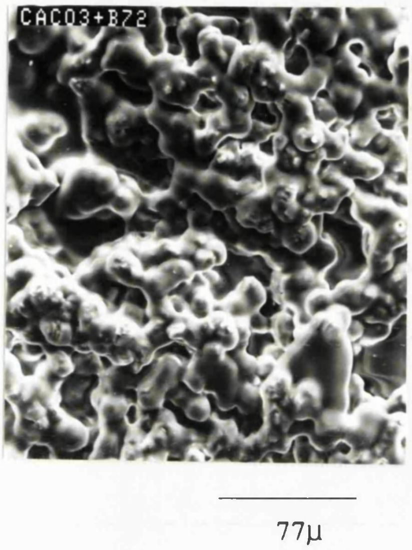


Figure 7.8 ~~sem~~ SEM photograph of calcium carbonate and Paraloid B72. sem

7.2.ii Subjection of samples to variable humidity conditions.

From the first set of experiments, it was discovered that all the salts had reacted similarly to the consolidants, namely that only the Paraloid B72 formed a visibly coherent layer over the salts. The next stage, therefore, was to discover whether the consolidants could prevent activation of the salts by water or water vapour present in a humid atmosphere.

Experiment design.

The same consolidants as in 7.2.i were used. However, it was decided for simplicity, to continue the experiments with salts that had no hydration states, namely sodium chloride, sodium nitrate and calcium carbonate.

The samples were prepared as in 7.2.i. The cured samples were then left in a humid environment (see 7.2.i) for 72 hours before being returned to a drier environment.

This set of experiments was repeated treating single salt crystals. If, at any stage in the experiment, more than one crystal appeared on the slide, this would be proof that the salt had been activated by water or water vapour.

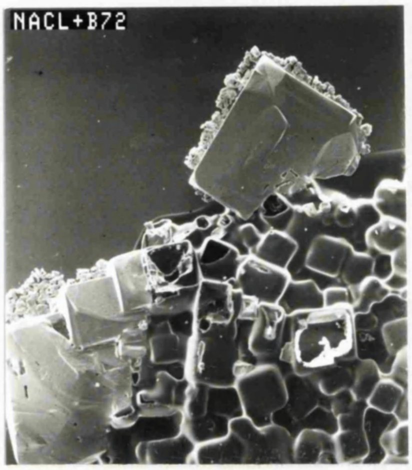
Results.

After exposure to the high RH, the calcium carbonate samples remained unaffected. This was to be expected, since the RH in the experiment did not rise above the equilibrium RH of the salt.

The sodium salts, though, were affected. The salts consolidated with the Wacker treatments dissolved in the high RH, and recrystallized in the dry environment. This was not a surprising result, since these consolidants had not provided a complete physical barrier to prevent access of water to the salts.

Analysis of the surface of salts treated with MTMOS had revealed the presence of some polymer. It would be interesting to discover whether this minimal surface coating could prevent activation of the salts. The experiments proved, however, that the hydration and crystallisation cycles of the salts were not prevented after treatment with the MTMOS.

Paraloid B72 was the only consolidant that formed a barrier capable of preventing salt activation. Surprisingly, though, in the high RH the salts dissolved under the B72 film, and some were redeposited outside the film when left in the drier environment (figure 7.9). When the treated single crystals were subjected to the RH fluctuations, multiple crystals formed, both underneath and outside the polymer film. The salts had not broken through the resin film, and the method of water entry and salt escape were not apparent. Therefore it was decided to investigate this situation further.



0.86mm

Figure 7.9a ~~sem~~ SEM photograph of sodium chloride and B72 after subjection to cyclic humidity conditions. Note that holes in the film were caused when sample was placed under vacuum in the ~~sem~~ SEM chamber.

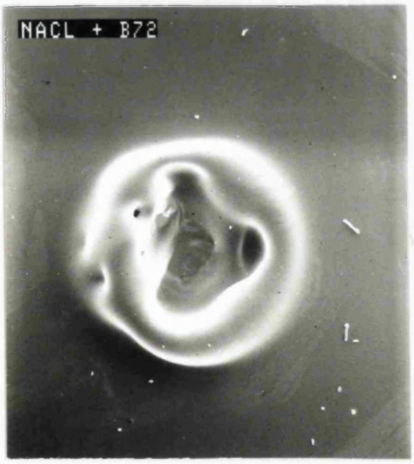


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Figure 7.9b Single sodium chloride crystal subjected to cyclic humidity conditions.

Figures 7.9c,d,e Close-up photographs of areas on 7.9b, revealing that the film has been stretched, but not torn.

7.2.iii INVESTIGATIONS INTO THE ACTIVATION OF SALTS TREATED WITH PARALOID B72.

The activation of the salts under a protective film of B72 can be divided into two stages, namely introduction of water or water vapour to the salts, and escape of the salts in solution from the film.

Plueddemann (1982) states that "water molecules diffuse through any plastic and will thus reach the interface ... exposed to a humid environment". The diffusion of a penetrant through a polymer depends on the relative mobilities of the penetrant molecules and the polymeric chain segments. These are affected by such factors as shape, size and concentration of molecules, component interactions, and temperature (Comyn, 1985). A polymer with a high degree of crystallinity or a high glass transition temperature (Tg) will be less permeable than polymers with lower Tg's or a more amorphous structure (de la Rie, 1992). Raising the temperature provides energy for a general increase in segmental motion, which increases permeability (Comyn, 1985).

Diffusion generally occurs in the direction from higher to lower concentrations. The rate of diffusion, called the rate of mass transfer or diffusion flux (J), is defined as the mass (M) diffusing through, and perpendicular to, a unit cross-sectional area of solid (A) per unit of time (t) (Callister, 1985).

$$J = M/At \qquad \text{Equation 7.1}$$

If the diffusion flux does not change with time, for example the diffusion of a gas through a plate of metal for which the concentrations of the diffusing species on both surfaces of the plate are held constant, a steady-state condition exists. This situation is represented graphically as a straight line (fig. 7.10).

The concentration gradient is dC/dx (Callister, 1985). The flux is proportional to the concentration gradient, and is defined by the equation:

$$J = -D \frac{dC}{dx} \qquad \text{Equation 7.2}$$

where D is the diffusion coefficient. This equation is known as Fick's first law of diffusion. The negative sign indicates that the direction of diffusion is from a higher to a lower concentration.

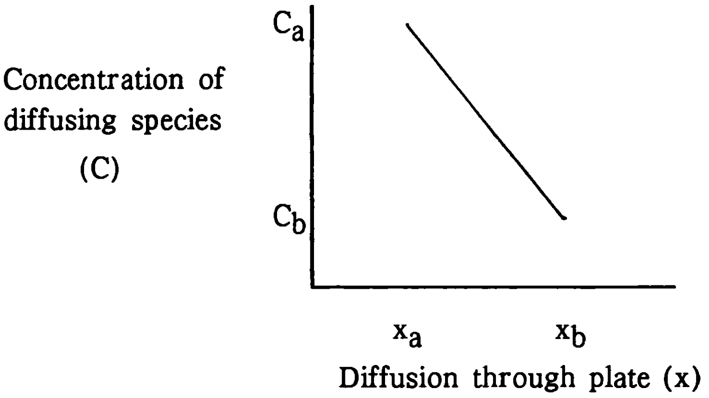

Figure 7.10 Graphic representation of steady-state diffusion (from Callister, 1985).

In nonsteady-state diffusion situations, there will be a net accumulation or depletion of diffusible matter in a unit volume, and the diffusion flux and concentration gradients will vary with time (Callister, 1985; Jastrzebski, 1987).

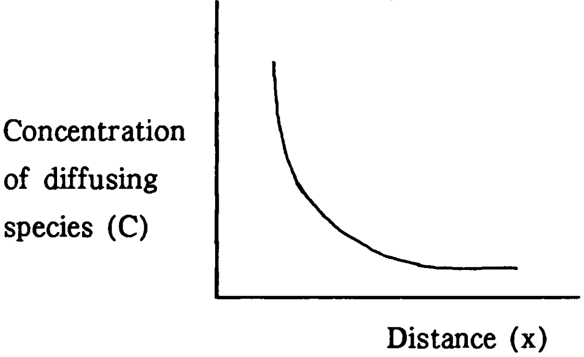

Figure 7.11 Graphic representation of nonsteady-state diffusion (from Callister, 1985).

Under these conditions, Fick's second law of diffusion applies, which is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right) \qquad \text{Equation 7.3}$$

In the situation of a sodium chloride crystal encapsulated by Paraloid B72, water vapour is passing through a polymer film from a humid environment to a drier environment (fig. 7.12a). As water vapour diffuses through the polymer, the salt will begin to dissolve (fig. 7.12b). Dissolution of the salt will continue until a saturated solution has formed underneath the film. Once the salt has fully dissolved, diffusion of water vapour through the film will continue, diluting the saturated solution (fig. 7.12c).

Full dissolution of a sodium chloride crystal (typically 30-50 microns (μ) in diameter) under a B72 film of approximately 5μ thickness took 72 hours.

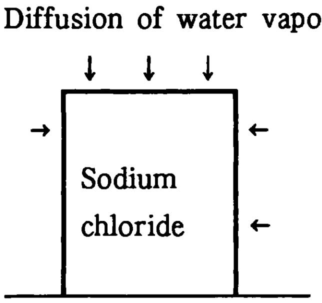

Figure 7.12 a Diffusion of water vapour through the polymer film.

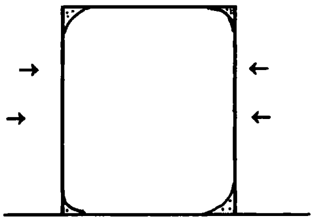

Figure 7.12b Salt crystal begins to dissolve under polymer film.

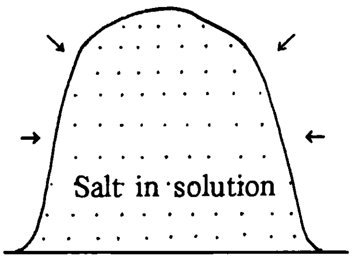

Figure 7.12c Salt in solution occupies greater volume than salt crystal, and stretches film away from surface of slide.

Release of salt solution from film.

Once the salt has dissolved, it does not break the film or seep through it. The salts crystallised around the edge of the film, as can be observed in figure 7.9a. To investigate the manner by which the salts escaped from the film, a sample was taken from a high humidity environment into the laboratory atmosphere and placed for observation the optical microscope. Using time-lapse videography, the sample was monitored as it dried.

To record the salt drying under the film, a system was developed as shown in the diagram below (fig. 7.13).

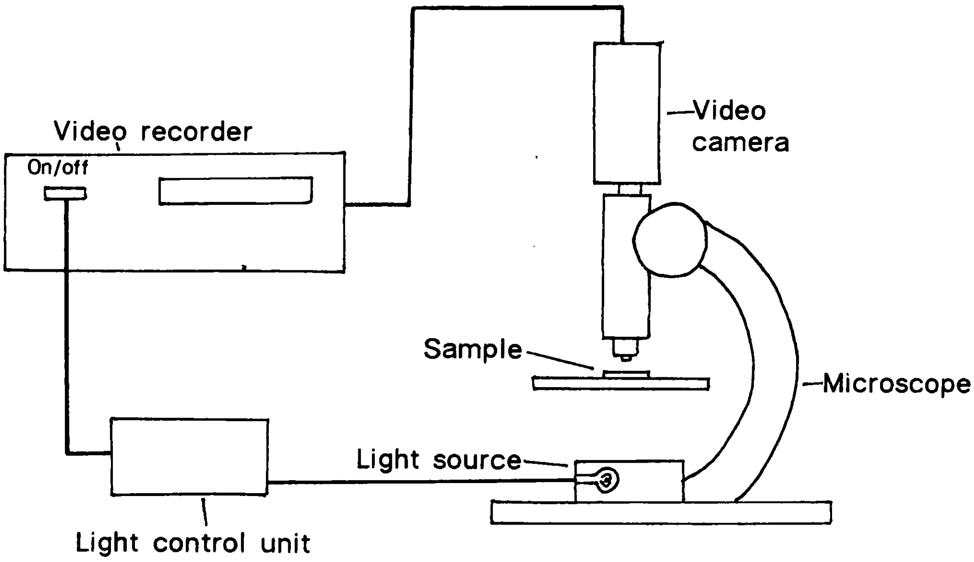

Figure 7.13 Diagram of the time-lapse video system.

Figure 7.14a Photograph of sodium chloride starting to recrystallise under B72 film after removal from high RH. Photograph taken from the video.

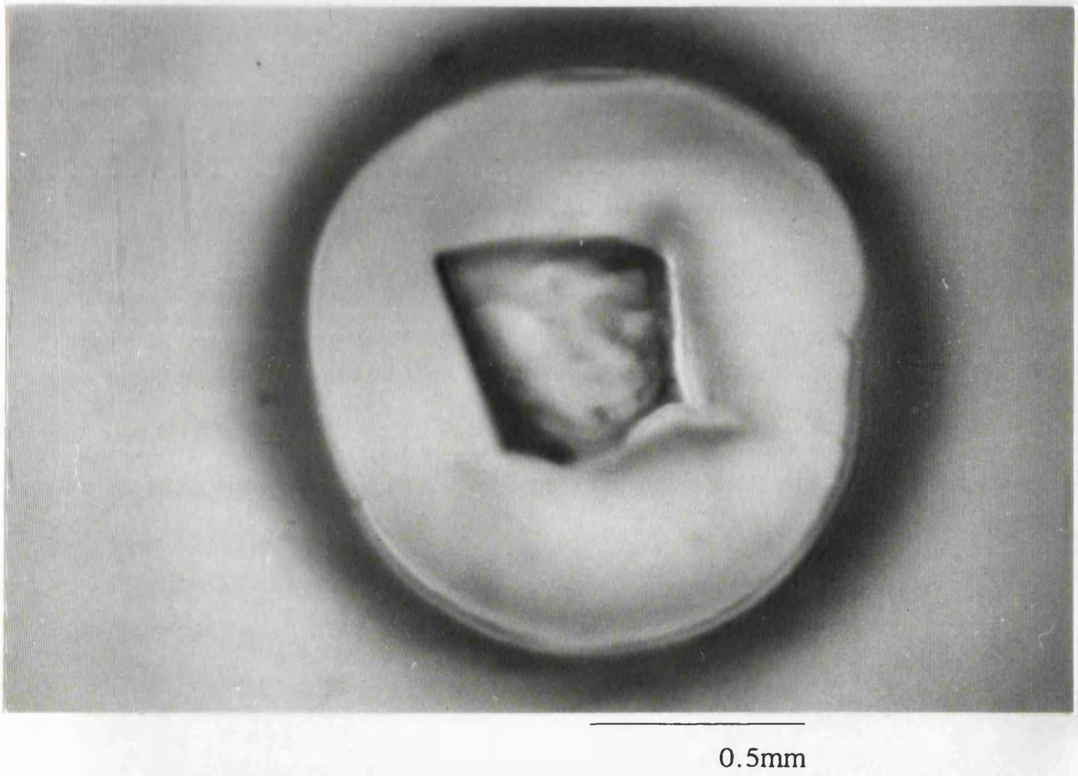

Figure 7.14b Photograph taken from video of sodium chloride recrystallising underneath B72 film.

d/

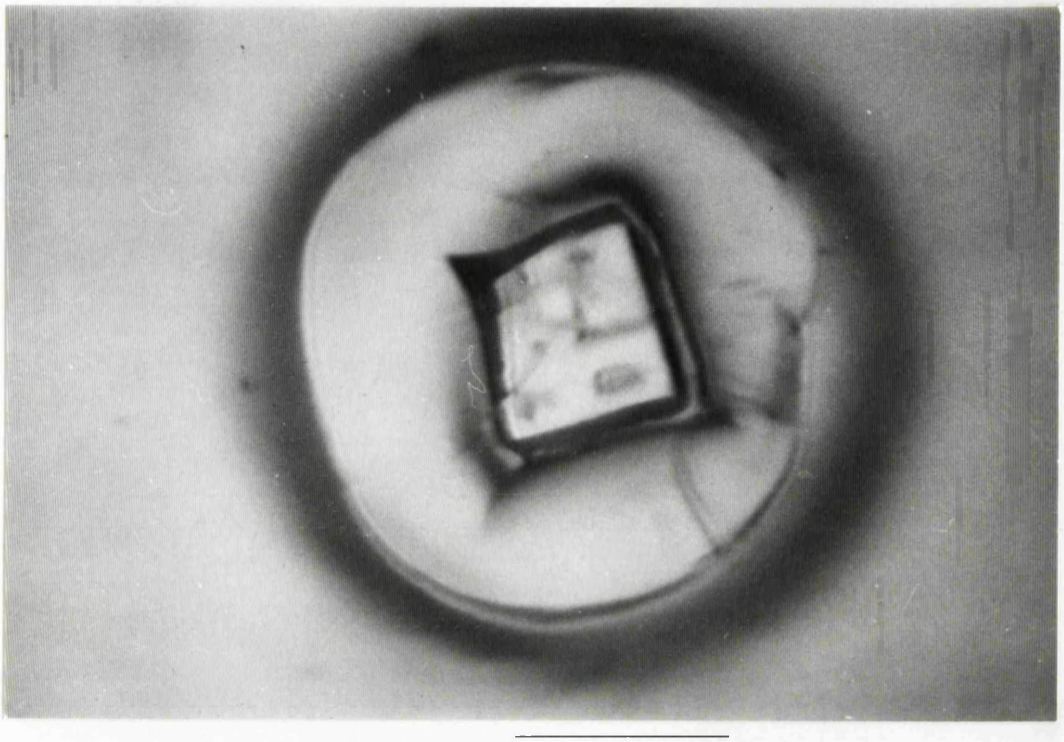

Figure 7.14c Photograph of recrystallised sodium chloride underneath B72 film. Note the collapse of the stretched B72 covering around the crystal.

The video recorder was programmed to record the view from the camera for 1 minute every 2 hours for 56 hours. However, if the microscope light were to be left on constantly, the heat from the light would affect the drying of the salt. Therefore it was necessary to develop a system whereby the light source in the microscope would be activated only during recording of the sample. This was achieved by the construction and use of a light-operated control unit. This unit consisted of a light-sensitive diode, which was attached to the video recorder's on/off button. This button lit when the recorder was recording, and activated the light-sensitive diode, which in turn switched on the control unit. The microscope light, which was routed through the control unit, was then triggered on. In this way, the microscope light was controlled by the video recorder, and was only switched on when recording was in progress.

The video recorded the recrystallisation of the salt from solution underneath the polymer covering. The volume occupied by the salt crystal is smaller than that of the salt in solution. The volume of a saturated salt solution can be much larger than that of the dry salt. For example, a saturated solution of sodium chloride has approximately seven times the volume of the dry salt. This increase in volume stretches, but does not tear, the B72 film. If the volume increase is large enough, the film is pulled away from the surface of the slide, and the salt in solution flows out from under the film. When the sample is placed in a dry environment, the salt recrystallises from solution outside the polymer film. In the video, the increase in volume produced by a single crystal was not enough to lift the film completely from the surface of the slide and allow the salt solution to escape from the film. As the salt recrystallised, the expanded film collapsed around the salt (figures 7.14a,b,c).

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Summary of experiments.

It was discovered that only one of the consolidants tested, Paraloid B72, was capable of forming a complete coating over the salts. When subjected to fluctuating humidity conditions, though, none of the consolidants prevented the absorption of water vapour by the hygroscopic salts. The object of encapsulation was apparently not achieved.

7.3 EXPERIMENTS INTO THE SOLUBILITY OF SALTS IN CONSOLIDANTS.

In chapter 5, the theoretical possibility of salts being soluble in consolidants and their solvents was considered. From the theoretical evidence, it was stated that in general, salts would not be soluble in the consolidants used in stone conservation. To test this theory, simple solubility experiments were performed.

To 10ml of consolidant 0.01g of salt was added and stirred. The results can be viewed in table 7.2.

	$NaCl$	$NaNO_3$	$CaCO_3$	$CaSO_4$	Na_2SO_4
Wacker H	i	i	i	i	i
Wacker OH	i	i	i	i	i
MTMOS	i	i	i	i	i

i = insoluble; ss = sparingly soluble; s = soluble

Table 7.2 Solubility of salts in consolidants.

None of the salts tested were readily soluble in the consolidants. It may be that smaller amounts of salts do dissolve in the consolidants, but for the purposes of this dissertation, it is sufficient to know that they are not readily soluble, and do not dissolve in large quantities. These results are concurrent with the theoretical predictions in chapter 5 (pages 62-69).

7.4 EXPERIMENTS INTO THE MOVEMENT OF SALTS IN CONSOLIDATED STONE.

Since the salts were not encapsulated, the next objective was to study the movement of the salts inside stone both during and after consolidation. Experiments were designed to establish whether salt movement in stone was hindered by consolidation or accelerated, as reported by Bradley and Hanna (1986).

7.4.i Experiment design.

This experiment design was based upon tests performed by Arnold and Price (1975).

The stone used in the experiments was an oolitic limestone with sparite cement. Porosity tests were performed on the stone as described by Ross & Butlin (1989). The stone had a porosity of 16.3 (±0.3)% and a saturation coefficient of 0.76 (±0.02).

The same consolidants as in 7.2.i were used, with the addition of a treatment of 1:4:3 water:MTMOS:industrial methylated spirits (IMS). This treatment was suggested by Wheeler et al. (1991) as the best silane-based mixture for the consolidation of marble. For each experiment, an untreated sample was included as a control.

The salt used in these experiments was sodium chloride.

Blocks 5x2x2 cm were cut from the stone. They were thoroughly washed and dried to remove any traces of soluble salts before being immersed in a 10% w/v sodium chloride solution for 24 hours, and dried again in an oven at 60°C for 24 hours. Oven drying was necessary to ensure the salts crystallised as subflorescence rather than efflorescence. After oven drying, the samples were left to achieve a constant weight in a controlled environment of approximately 44%

RH and 18-22°C (the RH was produced using a saturated solution of potassium carbonate).

The samples were consolidated by capillary absorption. This involved lying the samples horizontally in dishes to which enough consolidant was added to half-cover the stone. After the consolidant had fully penetrated the stone by capillary absorption, the samples were removed and returned to the controlled environment to allow the consolidant to cure.

The four long sides of each sample were then sealed with microcrystalline wax. This was done to ensure that any salt precipitation would occur only on the tops of the samples.

The samples were then stood vertically in a tray into which was added deionised water to a depth of 20mm. The level of water in the tray was kept constant throughout the experiment. The rate at which water and salt efflorescence appeared on the tops of the samples was monitored visually.

A duplicate set of experiments was run concurrently, with the addition of a non-ionic detergent (Synperonic N) to the deionised water. This was added to overcome the water repellency of some of the consolidants.

A third set of experiments was also run, with consolidated samples that had been desalinated but not resalted. Sodium chloride becomes hygroscopic at humidities greater than 77% RH (at 20°C). It is possible that as the RH within the stone rises in the presence of water, a hygroscopic salt will attract water vapour into the stone, and hasten the process of salt solution by increasing the rate at which water enters the stone. In this case water would reach the top surface of salted samples faster than in unsalted stones. These experiments were also designed as a comparison for the rate at which water, and salts in solution rose up the samples.

7.4.ii Results.

The average salt content in samples was 0.57 (±0.03) % by weight. The average percentage of consolidant in samples after curing is given in table 7.3.

	Paraloid B72	Wacker H	Wacker OH	MTMOS	MTMOS solution
Salt-laden	0.67±0.04	2.49±0.13	2.51±0.15	0.86±0.35	0.72±0.18
Salt-free	0.62±0.001	2.71±0.1	2.76±0.16	1.00±0.1	1.19±0.12

Table 7.3 Amount of consolidant (wt. %) retained by samples after curing.

Contact angle measurements.

The hydrophobicity of the salted samples was tested semi-quantitatively by observing water droplets placed onto the surface of the stone with a pipette. This was repeated on each sample to check the reproducibility of the results. The contact angles were measured by eye, and are given in table 7.4.

No treatment	Paraloid B72	Wacker H	Wacker OH	MTMOS	MTMOS soln
0°	>90°	>90°	0°	80-90°	~90°

Table 7.4 Contact angle measurement on surface of stone samples.

As expected, the water spread and wet the surface of the untreated stones and those treated with a non-hydrophobic consolidant. Regarding those treated with MTMOS, the water spread slowly and eventually wet the surface. With the treatments giving contact angles greater than 90° (the hydrophobic consolidants), there was a slight absorption of water into the pores of the stone. This is in contradiction to Shaw's ideas (1992) that the liquid will not penetrate into the pores when the contact angle is greater than 90°

(see 4.1.iii, page 50). It is possible that the water spread into unconsolidated pores in the stones.

Effect of salts on consolidation of samples.

A comparison between the amount of consolidant in salted and salt-free samples can best be achieved by analysing table 7.3. The Wacker treatments produced the highest yield of consolidant, nearly three times more than the other silane-based treatments. The Wacker products contain a neutral catalyst, dibutyltindilaurate, which accelerates polymerisation inside the stone before the silane evaporates (Wacker product information, Wheeler et al., 1991).

There was little difference in the quantity of consolidant retained in the samples treated with Paraloid B72. From the discussions in chapter 5, one would not expect the salts to affect consolidation by acrylic resins.

However, one would expect sodium chloride to adversely affect the treatments containing silanes, namely Wacker H, Wacker OH and the two treatments with MTMOS. Indeed, in the samples treated with Wacker and the MTMOS mixture, there is noticeably less consolidant in the salt-laden samples than the corresponding salt-free stones. The amount of neat MTMOS in the samples was too varied for such comparisons to be made. This in itself is significant, since it indicates that this method of consolidation may not be reliably reproducible.

Movement of salt through samples.

The time taken for efflorescence to appear on the samples can be seen in figures 7.15 and 7.16. Not surprisingly, efflorescence appeared first on the unconsolidated samples. What was surprising was the observation that efflorescence appeared on the tops of

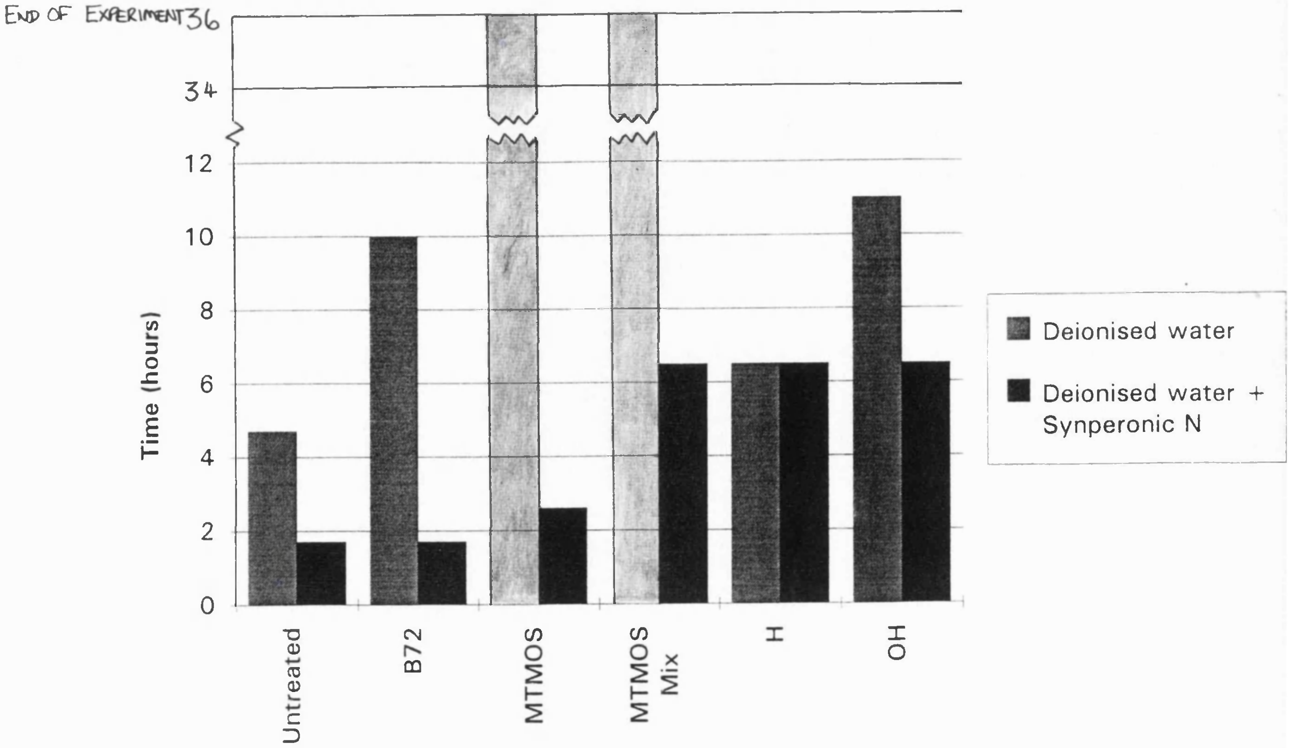

Figure 7.15 Graph to show time taken for water to appear on surface of unsalted samples

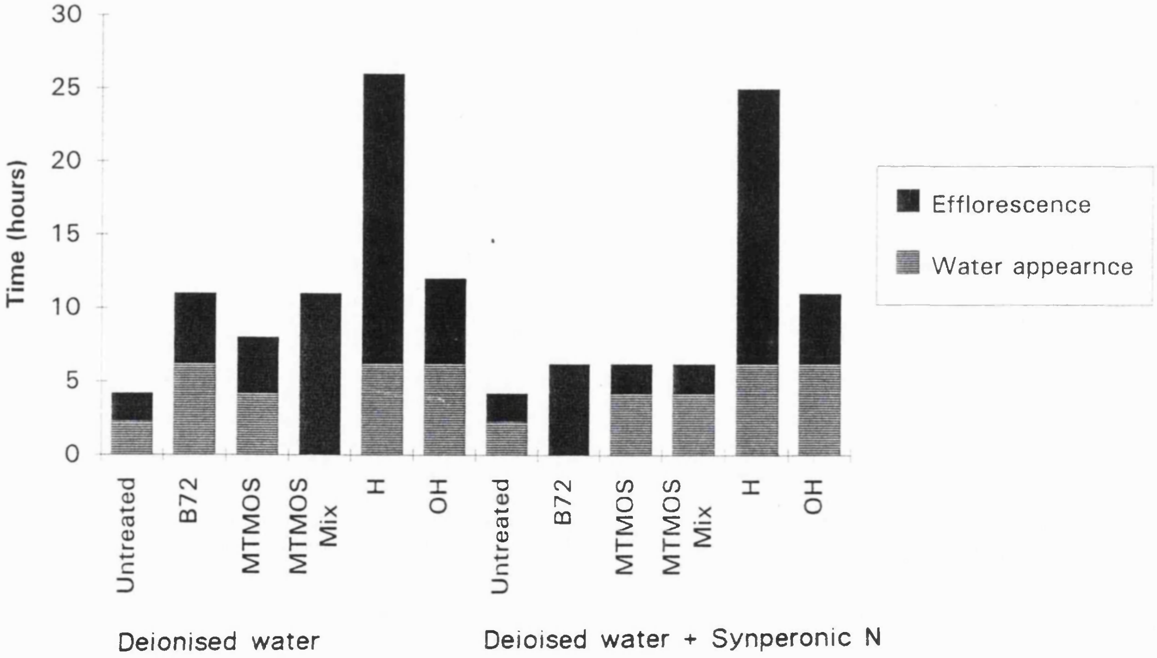

Figure 7.16 Graph to show appearance of water and efflorescence on surface of samples.

samples treated with hydrophobic consolidants when they were stood in deionised water alone. One might have expected the water repellency of these treatments to have prevented the penetration of liquid water into the stone. Water vapour, however, will diffuse through the stone.

Biscontin et al. (1981, 1985, 1986) conducted experiments into the water vapour permeability of consolidated limestone. All of the consolidants they tested reduced the permeability of the stone (Biscontin & Riva, 1981). At lower concentrations, Paraloid B72 inhibited permeability more than the silicone resin Rhône Poulenc 11309 (Biscontin et al., 1986). At concentrations of 30% or more of resin, the stone became saturated and the permeability constant. There appeared to be a connection between the concentration of consolidant applied to the stone and its permeability in that the permeability of the stone decreased as the resin concentration increased (Valle et al., 1985). The resin concentrations given in the reports reflect the amount of consolidant initially applied to the samples, and not the final amount left in the stone after curing. It would be interesting to compare the final consolidant concentrations with the permeability results. It is possible that the lower permeability of samples treated with Paraloid B72 may be due to the presence of a larger amount of acrylic resin in the stone inhibiting the passage of water vapour. It is important to remember that these results do not provide values for the water vapour permeability of the polymer films. The polymers do not fully block the pores inside the stone. To pass from one side of the stone to the other the vapour does not necessarily have to diffuse through the polymer film, but may pass through the narrowed stone pores (see fig.7.17).

Liquid water will also pass along pores that are not coated with a hydrophobic consolidant. These consolidants lower the surface free energy of the solid in air, preventing water from spreading along the surface. However, not all the pores inside the stone will be filled, or even lined with the consolidant. The weight of the samples increases

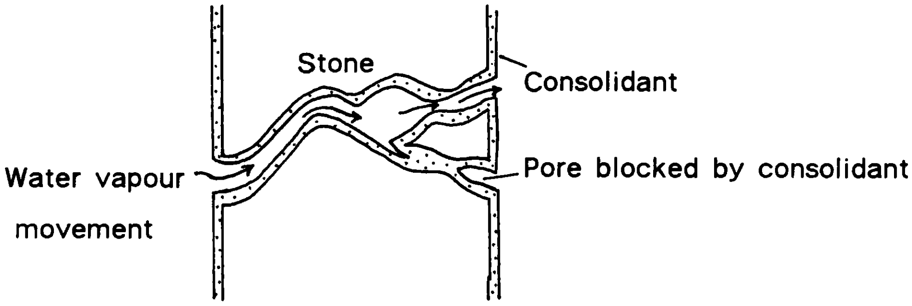

Figure 7.17 Passage of water vapour through narrowed stone pores.

by a maximum of 2.75% after consolidation, which is less than 20% of the pore space available. During the contact angle measurements, it was noticed that water droplets travelled into the pores of treated stones. Liquid water will, therefore, travel through unconsolidated or partially consolidated pores. It was discovered in the experiments above (see 7.2.ii) that the consolidants were not able to prevent dissolution of the salts. Water travelling through the stone would therefore dissolve the salts present in the stone, and the resulting solution would continue up the stone, eventually forming efflorescence on the upper surface.

The rate at which the solution travels will depend upon the size of pores, and the difference in surface energies of the solid/liquid and solid/gas interfaces. The size of pores will depend, in turn, on the extent of pore-blocking and pore-lining by the consolidants. It may be expected that the rate of transport will be affected by the concentration of polymer in the stone. This was not case in the experiments above. Salts were transported through the samples treated with Paraloid B72 at the same rate as those in samples treated with Wacker OH, which contained nearly four times as much consolidant. As stated in chapter 6, all of the polymers tested produce critical surface tensions lower than the surface tension of water. Sodium chloride will raises the surface tension further.

The type of polymer formed may affect the rate of transport. Valle et al. (1985) made the observation that when "poor" solvents are used to dissolve and apply a consolidant, "poorly permeable" superficial areas form where the resin is compact. These areas act as "discontinuous systems" and are "easily available to alterations, due to water and salt migration". This can "frequently cause the detachment of the whole superficial area". My interpretation of this information is that the polymers form clumps that block pores rather than creating a lining on the pore walls. These blockages reduce permeability more than narrowing of the pores (Valle et al., 1985). These areas, however, are readily detached from the surface of the stone by water movement, thus reducing the effectiveness of the consolidant as a strengthening agent. Paraloid B72 forms a lining along the pore walls, whereas silanes tend to form network polymers with filaments forming links between pore walls (Mavrov, 1983). Although there may be more silane polymer inside the stone, it is not wholly concentrated on the pore walls where it will most affect the progress of liquid transport through reduction of the critical surface tension.

A comparison of figures 7.15 and 7.16 shows that in the untreated sample and that treated with Wacker OH, water was detected first when salt was present. For the unsalted samples treated with MTMOS and the MTMOS mixture, no water was detected on their surfaces after 36 hours, when the experiment was stopped.

It is interesting to note the time difference between the initial appearance of water on the surfaces and crystallisation of salts. Treatment with Wacker H greatly increases the time taken for salt efflorescence after the appearance of water. This suggests that the consolidant is somehow impeding initial salt solution.

The position of efflorescence on the surface of the stones was interesting. On the samples treated with MTMOS and MTMOS in solution, salts formed on half of the top surface. This distribution pattern is related to the method of stone consolidation. The portion of stone fully immersed in consolidant contains a greater amount of cured consolidant. Salts crystallise preferentially on high energy surfaces. The MTMOS provides a low energy surface, therefore the salts will effloresce in the least consolidated areas. This phenomenon was not observed on the other samples.

7.4.iii Summary of experiments.

These experiments have shown that none of the consolidants tested was able to prevent efflorescence on the stone samples. The Wacker H produced the greatest delay. No real conclusions can be drawn about the rate determining step of salt uptake and movement in solution. The results raise some interesting questions about how Wacker H delays salt efflorescence so much longer than the other hydrophobic treatments.

The contact angle experiments show that water may remain as a droplet on the surface of stone, as proposed by Larson (1980), but will be absorbed into the stone over a period of months.

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8. CONCLUSIONS AND DISCUSSION.

8.1 INTRODUCTION.

This thesis has examined in detail the complex relationships that exist between various salts and consolidants connected with stone deterioration and conservation. In the following chapter, the information presented will be summarized, and the implications discussed using some practical situations as examples. Areas for future research will be highlighted. In this manner, it is hoped that the the relevance and importance of this work to stone conservation will be demonstrated.

8.2 DISCUSSION.

Let us begin with a discussion of a relatively simple situation comprising the interactions between a single salt crystal and a consolidant. Consider the salt crystal lying in an open pore within the top millimetre of the surface of a piece of stone, and in intimate contact with the stone (figure 8.1). Now consider the introduction of a liquid consolidant into the pores of the stone.

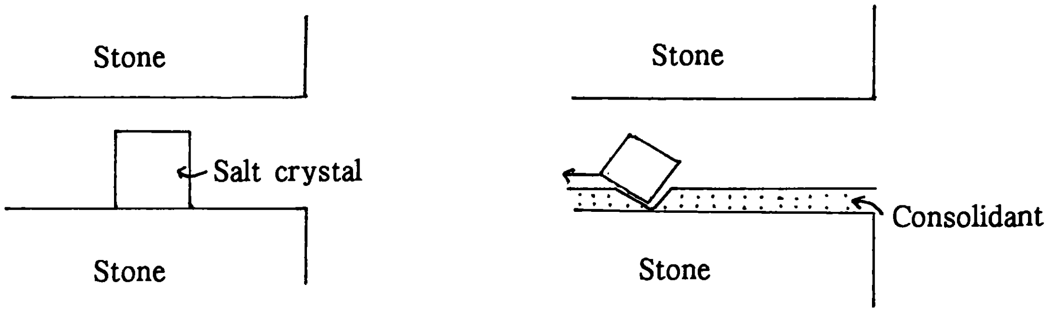

Figure 8.1 Introduction of consolidant into stone lifts salt from surface and transports it along with liquid.

If the interfacial energy between the liquid and the solid substrate γ_{sl} (in this situation stone) is less than the interfacial energy between the liquid and the salt, the liquid will preferentially spread along the surface of the substrate rather than the salt. If the interfacial energies between the liquid and stone and the liquid and salt are less than the interfacial energy between the stone and the salt, that is:

$$\gamma_{sl}(\text{stone}) + \gamma_{sl}(\text{salt}) < \gamma_{\text{salt.stone}}$$

the liquid may dislodge the salt from the surface of the stone. This phenomenon of the physical movement of salts by liquids was suggested by Pühringer and Weber (1990), and was observed in the experiments presented in chapter 7 (page 85). Only small particles were dislodged and moved around by the liquid. The energy differential for large particles was not great enough to allow their displacement by the liquid. Hence, in the scenario under consideration, the salt crystal may be physically dislodged by the consolidant, and may be carried further into the stone's pores with the liquid (figure 8.1b). If the salt is not in intimate contact with the stone, surface free energies do not govern the situation.

The possibility of the salt dissolving in the liquid was discussed in depth in chapter 5. Most salts commonly found in decayed stone are virtually insoluble in organic solvents. Many current consolidation techniques do not involve water as a solvent. However, some silane treatments use water as one of the solvents. This case merits special consideration. Let us take as an example sodium chloride in contact with a solution of methyl trimethoxy silane in deionised water and methanol. Upon initial contact, the sodium chloride will dissolve in the water, and will be transported in solution along the pores of the stone substrate. As the water is removed from the system, by evaporation or reaction with the silane, the salt will recrystallise. Sodium chloride has been shown to adversely affect the polymerisation of alkoxy silanes (Kumar & Price, 1994). Unfortunately, the use of water as a solvent in this case will ensure the presence of the salt during polymerisation of the silane.

Another interesting aspect to consider is the reaction between water produced during polymerisation of silanes, and salts. Water is produced from the dehydration condensation reactions of two silanol groups (see chapter 5, page 57). Wheeler reports that more silanols are produced in a mixture when there is more water present in the original system (Wheeler, 1987). Therefore a conceivable scenario is one in which a salt dissolves in the original water-silane system, crystallises as water is lost from the system, dissolves again in water produced from silanol condensation reactions, and finally recrystallises as this water evaporates. This scenario is dependent upon the system releasing enough water for solution of a salt.

As stated above, sodium chloride affects the polymerisation of methyl trimethoxy silane. The presence of salts affects the physical form of gel deposited (Iler, 1979). From figure 5.3, it can be seen that salts reduce the ionic charge on silica particles, permitting the formation of chains and gel networks. From a conservation viewpoint, this would be advantageous, since silica networks would strengthen stone without blocking pores. However, this advantage is counterbalanced by their negative effect on the polymerisation processes before gelation occurs. Goins (1995) discovered that the presence of soluble salts in alkoxy silane mixtures led to the formation of a weak particulate gel that she considered to be of little use as a consolidant. This area requires more research. With further study, it may be possible to elucidate specific trends regarding the effects of certain types of salts (for example sodium salts) on different forms of silanes. The effects of mixtures of salts is also an area requiring attention. Consider for example a mixture of two salts commonly found in decayed stone, sodium sulphate and sodium nitrate in contact with methyl trimethoxy silane. The rate of condensation of the silane is reduced in the presence of sodium sulphate, but increases when sodium nitrate is present (Kumar & Price, 1994). How would the condensation reaction be affected in contact with a mixture of the two salts?

If we now return to organic polymers, for example acrylic resins, there appear to be no chemical interactions between salts and these types of consolidants. The salts may be physically transported by the consolidant in its liquid state, but the salts will not affect curing of the consolidant.

The next major issue raised is where do the salts crystallise during any interaction? This is a matter of immense importance, requiring a detailed analysis of the situation.

Let us consider again the single salt crystal in a stone pore which is treated with a consolidant. If the crystal is dislodged by the incoming liquid, where will it be redeposited? Experience from the experiments in chapter 7 suggests the salt will be transported into the stone with the consolidant. With a consolidant that cures by solvent evaporation, the salt will be deposited when the consolidant begins to gel, possibly being sealed within the solid polymer matrix formed. With consolidants that cure by polymerisation, the salt will be deposited when a gel formation stage has been reached. Where this occurs inside a piece of stone depends upon the movement of the liquid through the stone. It is known that consolidants experience a backward movement as solvents evaporate (Horie, 1987). It is possible that salts from deeper within the stone may be moved towards the surface during this backward movement, producing a greater concentration of salts towards the surface of the stone.
Similarly, if salts are carried further into the stone, they may be left at a greater depth inside the stone. This movement requires further research to ascertain the extent of salt movement upon initial application of a liquid.

Let us now reconsider the situation of a salt dissolving and recrystallising in a silane-water mixture. After dissolving in the liquid consolidant, the salt in solution will be transported with the liquid. As water is removed from the system, the salt will be deposited in-situ. After further solution, a new surface, that of the gel will have formed. The question is whether the salt will crystallise from solution on the gel, or on the stone. Salt crystallisation occurs preferentially at high energy points in a system, which in this case is the stone surface. Therefore the salts will recrystallise preferentially on the stone rather than the polymerised silane.

If we now think about the relationships between salts and organic polymer consolidants, we will notice that initially there are no chemical interactions between the two components. The experiments in chapter 7 (page 85) have shown that it is possible for Paraloid B72 to form a covering over salts. More research is needed to discover whether such an intact polymer film forms inside stone pores, and over salts lying in stone pores. When the salts are activated in high humidities, the increase in volume of the salt solution stretches the polymer film. If the volume of solution is large enough, the salt solution escapes from between the film and the substrate. Even if the solution does not break the film, and the salt recrystallises under the film, subsequent solution and crystallisation cycles may weaken the film , causing it to tear in time.

The subsequent movement of the salt solution is of major importance, and is relevant to all types of consolidation. Let us imagine the situation in a pore where the stone has been consolidated, but a flawed film or a network of filaments has formed around the salts. Upon dissolution, a situation may arise where salt solution droplets will be forced to spread over the consolidated surface because of their volume.

As stated above, the solution will spread preferentially along the stone surface, and salt nucleation will begin on the higher energy surfaces (the stone). An interesting sideline would be to examine which minerals within a stone matrix provide suitable nucleation sites for salt propagation. If enough liquid is available, the possibility arises that the salt solution will travel into unconsolidated areas within the stone, as described in chapter 6. This may develop over a period of time, as the salts gradually travel in solution through the stone. This phenomenon has serious consequences for stone conservation. This thesis has demonstrated that consolidants do not prevent salt activity in stone. If a stone object has a salt problem, partial consolidation of areas is liable to transfer the salts to unconsolidated areas if salt activity has not been inhibited by other means. Hence stone decay due to salts will continue unabated in a different area.

In chapter 6, the desalination of consoldiated stone was discussed. From experiments in chapter 7, the movement of salts in consolidated must now be considered. As stated in chapter 6, the water introduced during desalination will travel preferentially along unconsolidated or poorly consolidated pores. It is conceivable, however, that the RH in the consolidated pores will be raised above the equilibrium RH's of some salts. If this occurs, and the salts dissolve, the question of their movement is important. If enough water is introduced to dissolve the salts, the solution may flow into unconsolidated areas and be drawn to the surface. If a limited volume of water is introduced, it is possible that the salts will recrystallise in situ within the consolidated areas. In this case, desalination will not be successful. Therefore, it is important to use enough water to achieve adequate desalination of consolidated stone areas. The quantities of water necessary are unknown. This is an interesting topic worthy of future investigation.

The discussion so far has concentrated on the interactions between salts inside stone and consolidants applied to the stone. Imagine a situation in which the stone has been desalinated and consolidated, but is open to further salt ingress. The factor to ascertain is where the salts will be deposited in the stone. This will depend in part upon the method of entry of the salts into the stone.

If the salts travel in solution by capillary action from ground water, it is conceivable that the solution will travel through unconsolidated pores, bypassing consolidated areas. It thus follows that any salt deposition would be in unconsolidated areas. This type of movement and deposition through consolidated stone was demonstrated in chapter 7 (page 85). The salts were deposited on surfaces with less consolidant.

If the salts form on the surface of consolidated stone, by processes described in 2.1.iii, their movement is more difficult to predict. Soluble salts may be carried into the stone in solution. Again, the solution will follow the path of least resistance, that is preferring a route through unconsolidated or partially consolidated pores.

Another aspect is one in which salts from deeper inside a treated stone are activated. These salts may be activated by a deep penetration of water, and will be carried towards the surface of the stone by capillary action. From the discussions above, it is likely that the salts will crystallise in unconsolidated pores. If the surface of the stone was heavily consolidated, the salts would crystallise at the interface between consolidated and unconsolidated areas, leading to subflorescence and spalling of the consolidated layer as the interfacial area was weakened by salt action. In a lightly consolidated stone, the salts would crystallise within the consolidated layer, but would tend to be concentrated in unconsolidated ~~areas~~ pores. More practical work is necessary on this subject to determine the relationships suggested here.

8.3 CONCLUSIONS.

This thesis has examined in depth by theoretical considerations and practical experimentation the possible relationships between salts and consolidants during the consolidation process in stone. These relationships are as varied and complex as the two groups under consideration.

In general terms, both salts and consolidants are affected by each other. Some salts affect the polymerisation and curing processes of some consolidants. Conversely, consolidants affect the position of salt crystallisation within stone. Consolidation does not prevent salt activity, and the presence of salts can adversely affect the quality of consolidation achieved.

These issues are of importance to stone conservation. It is important to realise the consequence of consolidating salt-laden stone. Consideration must be given to the future movement and activity of salts. Furthermore, it has emerged from this thesis that consolidation affects desalination of stone from two angles. Firstly, the position of salts in stone may be redistributed by consoldiation. The consolidant then affects entry of water into the stone.

This dissertation has highlighted the relationships between salts and consolidants. It has also discovered areas where there is potential for more research, which is necessary to provide a clearer picture of the interactions between salts and consolidants.

8.4 REFERENCES.

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APPENDIX 1.

When comparing salt analyses from different sources, it is important to note what material the analysis was carried out on. In some articles, analysis is performed on samples of the decayed stone (for example Saleh et al., 1992); in others, aqueous extracts from the stone are analysed (for example Bradley & Hanna, 1986). In some cases, both types of analysis are performed (Arnold et al., 1986; Livingston, 1994).

The different methods will produce different results. Analysis of aqueous extracts will provide details of the soluble salts in the stone, and hence those which are extractable by desalination. However, any sparingly soluble salts may not be detected. Due to the potential effects of salts on each other, and on consolidation treatments, it is important to acquire knowledge of all salts present.

Analysis of only crystalline deposits may also not provide an accurate representation of all the salts present. From a comparison of the two techniques used by Arnold et al. (1986) in the Müstair Convent, Switzerland, it can be seen that although a high concentration of chloride ions was found in the aqueous extract, no crystalline chloride deposits were discovered on the walls. This is most probably because the chlorides were in solution when samples were taken.