The encapsulation of salts by consolidants used in stone conservation

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Introduction

Stone has been used by man as a building material, and for sculpture, for thousands of years, because of its relative strength and durability. However, since the onslaught of industrialisation, the built environment has been subjected to increasing rates of decay. This has been met with a growth in conservation treatments. One of the aims of stone conservation is to prevent deterioration of the stone by the action of soluble salts present in the decayed stone. One approach is to encapsulate the salts in a consolidant, thereby suppressing their activity. This was one of the objectives when deeply penetrating consolidants were first investigated in the early 1970's. However, it transpired that some objects were still exhibiting efflorescence after consolidation. The aim of the work described in this paper was to undertake an investigation into the encapsulation of soluble salts by consolidants commonly used in stone conservation.

Role of soluble salts in stone decay

The decay of stone is a complex procedure, involving many different mechanisms. One major element is the deterioration caused by the action of soluble salts in the stone. The salts come from a variety of sources:

1) some soluble salts are inherent in the original stone matrix;
2) they may have been produced as a result of the breakdown of other constituents. An example of this type of salt formation is the action of acidic airborne pollutants on calcareous stones. Sulphur dioxide and carbon dioxide dissolve in water droplets to form acidic solutions. These acids are deposited on the stone with the water when it comes into contact with the stone, as rain or mist; they react with alkaline components in the stone, such as calcium carbonate, and a soluble salt is formed. Biological agencies, such as bacteria, fungi and lichens also produce acids that attack the stone to produce soluble metal chelates, which the organism can then utilise as nutrients (Ganorkar et al. 1987);
3) the salts may have been introduced from an external source. Ground water rising through a building (rising damp) carries with it nitrates and phosphates from the soil.

Once inside the stone, the exact mechanisms by which soluble salts cause decay are not fully understood. There are a number of possible explanations. When a soluble salt is formed by other decay processes, it may be of a different

size than the original stone component. If the salt is smaller, it will leave a void in the stone matrix. If the salt formed is of a larger size, it will create stresses on the surrounding stone structure. Both formations will weaken the stone. If the salts formed go into solution, they may be transported elsewhere in the stone. The salts may recrystallise out of solution on the surface of the stone, a phenomenon known as efflorescence. This can be removed by brushing the salts off the surface, if a hard concretion has not formed, and the salts will take no further role in the stone's deterioration. A more destructive process is the deposition of the salts inside the stone, called subflorescence. It is thought that as the salts crystallise out of solution, the crystallisation pressures created generate forces that disrupt the intergranular contacts in the stone (Lewin 1976; Winkler 1971). Cycles of dissolution and crystallisation of the salt crystals inside the stone may severely affect the strength of the stone, leading to spalling of the layer beneath which the salts are active (Bradley 1985).

Some salts do not have to fully dissolve into solution to weaken the stone, for example salts with multiple hydration states. Every change in hydration state produces a corresponding volume change, severely disrupting the internal structure of the stone. The rate of hydration may also be an important factor (Knöfel *et al.* 1978).

Prevention of soluble salt action

One of the objectives of stone conservation is to prevent further damage occurring due to activities of the soluble salts. In artefacts with a salt problem, this may be achieved by:

      1) removing the salts from the stone;
      2) controlling the conditions governing their movement;
      3) encapsulating them in a consolidant, thereby inhibiting further movement. (Bradley 1985; Puehringer and Engstrøm 1985; Skibinski 1989).

Removal of salts, desalination, is a practical solution for small artefacts that can be soaked in a water bath. However, this is not an option for larger works in stone. Poulticing is a technique often used on buildings. Experiments have concluded, though, that only the outer 20mm of a surface can be desalinated using poultices (Bradley and Thickett 1992). Salts deeper in the stone remain untouched. In addition, outdoor structures face the continual influx of soluble salts, from ground water and acid attack. Therefore poulticing would have to be a continuous process.

The second option is again quite easy to fulfil for small objects that can be stored in a stable environment. Control of the relative humidity (R.H.) around the object should prevent the hydration and crystallisation cycles of the salts. On large outdoor monuments, water repellents have been applied to the stone's surface in an attempt to prevent the ingress of water, and thus prevent salt activity. One group of materials used was silicone resins. These contain two functional groups useful for stone conservation. The Si-O groups chemically

attach themselves by hydrogen bonding to the stone's surface, whilst the methyl groups provide water repellency. In practice however, only a thin layer forms on the surface with enough spaces between silicone molecules to allow the passage of water vapour, which will activate the salts underneath (Torraca 1984).

The third possibility, encapsulation of the salts with a consolidant, would be an ideal approach. The consolidant would be fulfilling the criteria of both strengthening the weakened stone and inhibiting further salt movement. To achieve encapsulation of the salts, the consolidant should ideally produce a lining around the grains of the stone and the salts without filling the pores, thus allowing excess water to leave the stone without affecting the newly immobilised salts (Bell and Coulthard 1988; Hanna 1984). It was believed in the early 1970s that silane and silicone-based consolidants were encapsulating the soluble salts inside the decayed stone (Moncrieff 1976). However, some conservators noticed that after consolidation with silane-based products, objects that were being stored in a stable environment were still exhibiting efflorescence, which was often occurring more rapidly than before treatment (Bradley 1985; Bradley and Hanna 1986; Larson 1980). These observations suggested that the salts were not being encapsulated.

A small amount of research has been conducted in this area. Mavrov discovered that some silicone-based products did not prevent the movement of sodium sulphate inside treated stone (Mavrov 1983). The aim of my work was to investigate further the encapsulation of a range of salts by consolidants commonly used in stone conservation.

Experiment design

Experiments were designed to discover whether a range of consolidants commonly used in conservation formed a coherent layer that was able to physically encapsulate a range of salts. The consolidants tested were:

> 1) Paraloid B72 (20% w/v in toluene);
> 2) Wacker OH, a 'one-component system' based on silicic ethyl ester (Wacker product information leaflet);
> 3) Wacker H, a 'one-component system' containing a silicone to impart water repellency, and ethyl silicate to strengthen the masonry material (Wacker product information leaflet);
> 4) Methyl trimethoxy silane (MTMOS).

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

The soluble salts chosen as representative of those found in decayed stone were sodium chloride, sodium sulphate, anhydrous calcium sulphate (anhydrite) and calcium sulphate dihydrate (gypsum). The tests were also performed on calcium carbonate, since it is the main constituent of limestone.

For each salt and consolidant combination, a small amount of salt was placed on a microscope slide and covered with a few drops of consolidant. The prepared slides were placed in ambient laboratory conditions (18-22 °C, 40-50% R.H.) to allow the consolidant to dry/polymerise, and examined using optical and scanning electron microscopy. The samples were then placed in a sealed chamber at 85% R.H. for 72 hours, before being returned to a dry environment (10% R.H.). This part of the experiment was designed to test the ability of the consolidants to prevent activation of the salts by water vapour present in a damp atmosphere. Changes in the samples were again monitored using optical and scanning electron microscopy.

Results and discussion

Table 1 reveals the ability of the various consolidants to form a film on the salts before exposure to high R.H.

	Sodium chloride	Sodium nitrate	Sodium sulphate	Calcium carbonate	Anhydrous calcium sulphate	Calcium sulphate dihydrate
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
MTMOS	no covering visible	no covering visible	no covering visible	no covering visible	no covering visible	no covering visible
Paraloid B72	intact film formed	intact film formed	intact film formed	intact film formed	intact film formed	intact film formed

Table 1. Performance of consolidant films on various salts.

As can be seen in Figures 1 and 2, Wacker H and Wacker OH formed thin cracked films on the surfaces of the different salts. The films had cracked at the interface of the salt and consolidant, and in between the salt crystals. When handled, the Wacker OH film appeared to be more brittle than the film formed by Wacker H. The Wacker OH failed to hold the salts on the slide (Fig. 3). In areas where the Wacker consolidants had polymerised and no salts were present, intact films with no flaws had formed. The movement of the salts was not prevented when the samples were subjected to the changes in humidity. Therefore, these consolidants had not encapsulated the salts.

When examining the salts treated with MTMOS, no film could be seen on the salts under the optical and scanning electron microscope (see Fig. 4). It appeared that the consolidant had mainly evaporated before polymerisation. EDAX

analysis of the surface of a treated sodium chloride crystal revealed a very small amount of Si present, which was sparsely distributed over the crystal's surface. In the changing humidity conditions, the polymerised silane present on the salts did not prevent the hydration and crystallisation cycle of the salts. Therefore, the salts were not encapsulated by the MTMOS.

The only consolidant tested that created a continuous layer over the salts with no flaws was Paraloid B72 (Fig. 5). After exposure to high RH, the calcium salts remained unaffected. This was to be expected, since the RH in the experiments did not rise above their equilibrium RH's. However, the sodium salts had been redeposited outside the B72 film (Fig. 6). Further investigations using single salt crystals covered with B72 revealed the mechanisms by which these salts had escaped from the film. In high RH, water vapour diffuses through the B72 film. The salt began to dissolve in the water vapour and a salt solution form under the film. Full dissolution of a sodium chloride crystal (typically 30-50 microns across) under a B72 film of thickness approximately 5 microns took 72 hours. The volume of a saturated salt solution is larger than that of a dry salt. A saturated solution of sodium chloride, for example, has approximately seven times the volume of the dry salt. This increase in volume stretches the B72 film, but does not cause the film to tear. Instead, the film is pulled off from the surface it is on, and salt in solution flows out from the film. When the sample is placed in a lower RH, the salt recrystallises from the salt solution.
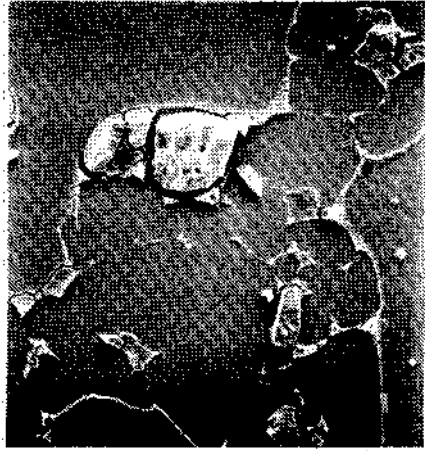

20kv -------------------- 231μm

Figure 1 SEM photograph of sodium chloride treated with Wacker H
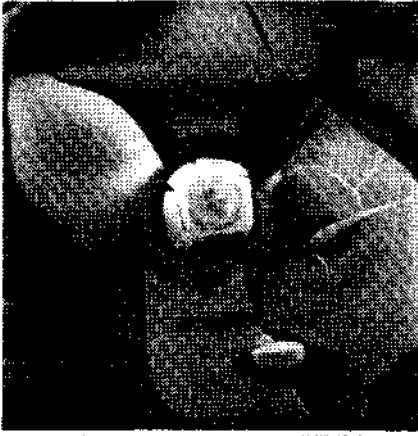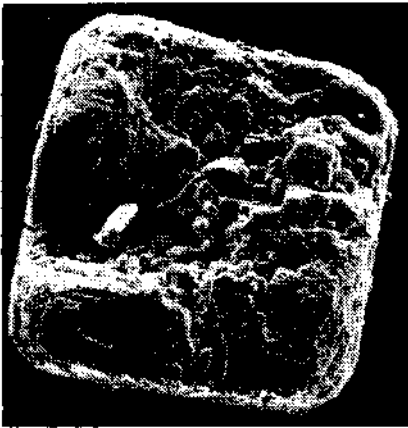
20kv -------------------- .86mm
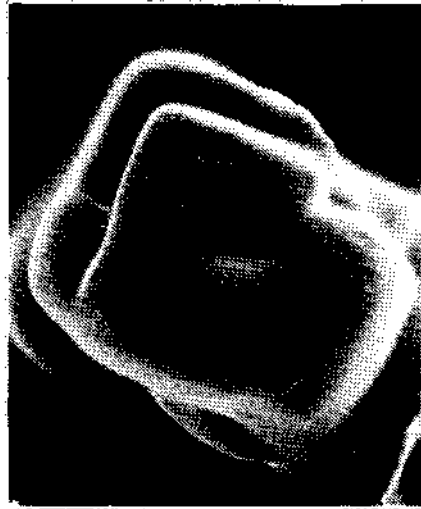**Figure 2** SEM photograph of sodium chloride treated with Wacker OH

20kv ----------------; .60 mm
Figure 3 SEM photograph of sodium nitrate treated with Wacker OH

20kv --------------------- 231 μm
Figure 4 SEM photograph of sodium chloride treated with MTMOS

20kv -------------------- .27 mm
Figure 5 Sem photograph of sodium chloride treated with Paraloid B72
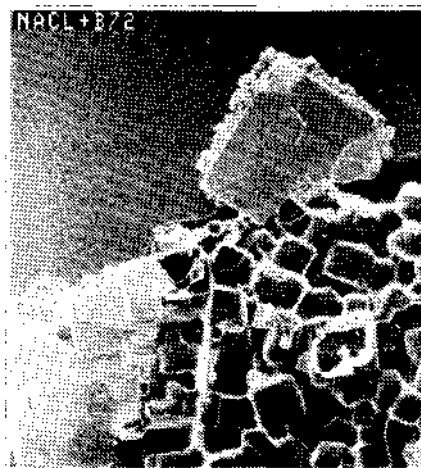
20kv |------------------| .86 mm

Figure 6 Sem photograph of sodium
chloride treated with Paraloid B72,
after being in high RH (see note 1)

Conclusions

Under the conditions of this experiment, none of the consolidants tested
prevented the absorption of water vapour by the hygroscopic salts. The objective
of encapsulation was apparently not achieved. It is realised that these experiments
do not represent the real situation when a consolidant is applied to decayed stone.
The relationship between the stone, and the salts and the consolidant must also
be taken into consideration. Research into these interactions is currently in
progress.

Materials

MTMOS supplied by: Dow Corning, Kings Court, 185 Kings Road,Reading
RG1 4EX. Tel: 0734 507251.

Wacker H and Wacker OH supplied by: Biokil Chemicals Ltd. Brickyard
Industrial Estate, New Yard, Gillingham, Dorset SP8 4BR. Tel: 0747 823121.

Note 1

The tears visible are due to rupture of the film when the sample was carbon-
coated under vacuum before SEM examination.

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