



1. Overview

Deep consolidants, surface consolidants, and pre-consolidants have been used by conservators to try and help:

- a)** strengthen decayed stone where there has been a failure of the stone binder because of weathering, atmospheric pollution or through inappropriate intervention
- b)** minimise the rate of stone decay
- c)** to provide temporary/reversible emergency support for vulnerable areas before full scale analyses and treatments can be carried out

in the past 30+ years many materials have been used with varying degrees of success on stone but no single method has been found to be successful on all stone types

This lecture is focussed on *deep consolidation*.

2. General criteria for consolidation

Before any treatment to an object the conservator should understand:

- a)** the levels of dirt and the desired level of cleaning for the object
 - b)** the stone's geology
 - c)** history of previous treatments
- and where possible
- d)** identify any similar previously consolidated objects and to assess the performance of the treatment
 - e)** complete a relevant literature survey for information of treatments used on similar stone types
 - i)** such a survey will typically allow the conservator comparative information and outline the particular problems associated with certain combinations of consolidants and stones
 - f)** determine the future care of the object
 - g)** ensure all relevant processes are comprehensively documented for future reference

3. General criteria for deep consolidation

The following performance criteria should be met in the selection of a suitable deep consolidant

- a)** the treatment should re-establish cohesion between the elements of the disaggregated stone
- b)** treatment should be generally compatible with the stone type
- c)** treatment should penetrate the stone to at least 25 mm or to the depth of stone deterioration
- d)** treatment should not prevent other treatments (eg. desalination and cleaning)
- e)** treatment should have low viscosity, moderate surface tension, low molecular weight and low reactivity within the first few hours following application to help penetration of the treatment into the stone
- f)** treatment should be capable of withstanding a wide range of temperature variations and exhibit a suitable glass transition temperature (T_g)
- g)** treatment should have a limited effect on both porosity and moisture transfer, and not create an impermeable zone between the treated and untreated parts of the stone
- h)** treatment should alter the deteriorated stone so it exhibits similar properties as far as possible of the sound stone

i) treatment should not cause permanent chromatic or reflectance changes to the stone and it should not discolour over time

- consolidants such as alkoxysilanes will discolour the stone for the first few months but these generally lighten up back to near the original stone colour – tests should be undertaken before full treatment where possible.

j) treatment should not be vulnerable to attack by salts, acid rain, atmospheric gases and pollutants, nor biological organisms – this information can generally be found in the literature

k) treatment should weather at a similar rate to the sound stone

l) treatment should have a low solvent content (for safety and ecological reasons)

m) treatment should have good adhesion eg. for fissure bridging



When talking about deep consolidation in relation to conservation ethics ideas such as **minimal intervention** and **reversibility** are better interpreted as *non-permanence*.

Remember, consolidation is generally a last-resort, used only when other treatments have not worked.

It is also advisable to include the possibility of re-treatment when searching for a suitable candidate.

4. Deep consolidant types

a) ethyl silicates – silane family

i) generally organosilicon compounds polymerise to form networks of silica gel - as the gel dehydrates it forms deposits of silica in the stone similar to natural silica deposits which cement the quartz grains in many sandstones.

ii) water vapour in the stone is needed as a catalyst – but if the humidity is too high it can cause a too rapid a reaction, and too much water leaves little space for the polymer to form

- briefly, silanes are hydrolyzed by water to form silanols, which then polymerize in a condensation reaction to give a silicone polymer. the water may come from the atmosphere or from the stone itself. a catalyst is usually in the form of an organotin or lead compound. the condensation and hydrolysis reactions take place after the silane has been absorbed by the stone and the resulting polymer consolidates the stone.

iii) silanes were developed for use with chemically similar sandstones but have been used with materials exhibiting a low chemical affinity to silica-based systems such as some limestones see right side image above from consolidation at the University of Cambridge. We'll discuss this below.

iv) silane-based materials are generally able to penetrate relatively deeply into stone although results depend on the stones porosity and application method and environment

v) silanes need careful application with curing period of 21 days absolutely necessary 'before the second 'topping up' application as the silica gel formation can break down in the presence of silane vapour during any re-application of consolidant

vi) porosity, water absorption and pore size distribution are affected by treatment to varying degrees and this influences resistance to salt crystallization and freeze/thaw action

vii) silanes are stable and will not break down in UV light or when exposed to acid rain. generally they produce a colour change which usually lessens within several months – the darker the stone the more noticeable the colour change as the refractive index is altered.

viii) silanes have been the most widely used stone consolidants over the past 25 years and two compounds, in have been dominant: methyltrimethoxysilane [MTMOS] which has a degree of water repellency, and the higher polymer-yielding tetra-ethoxysilane [TEOS] which has little water repellency - water repellency is not always desirable and can lead to unwanted zones (see 3 g) above).



re. limestone - in general silanes do not bond well to calcite, the main mineral in limestone, (however, sometimes consolidating limestones with silane does work!)

As such, pre-treatments exist to prepare the calcite in limestones to receive the silane.

One treatment, called Hydroxylating Conversion Treatment (HCT), is a two-component, waterborne treatment which is useful for consolidating deteriorating limestone, by not only etching the calcite to receive the silane – done with ammonium tartrate - but also by having its own consolidating effect by precipitating calcium tartrate tetrahydrate (CTT).

In the image we can see it applied to chalk.

b) acrylic consolidants:

i) Although in situ polymerization of acrylics on stone has been tried and some increase in strength reported, they are generally not considered successful as consolidants.

They include methylacrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, and polymethyl-methacrylate (PMMA).

ii) Far more attention has been given to the use of acrylic resins dissolved in solvents, and Paraloid B72 (or Acryloid B72 in the USA), a copolymer of methacrylate and ethyl methacrylate is often used as it is chemically stable, reversible, and does not yellow with age – it has been used outside for a long time as a stone consolidant but with variable results.

Generally B72 is used in the consolidation of wall paintings (1-5% solutions); ground and pigment layers on oil paintings (5-10% in either toluene or isopropanol); fragile wood in furniture, polychrome on sculpture (5-20%); to consolidate wooden artifacts; to consolidate plaster; as a fixative for chalk, charcoal and pencil marks (2-4% in toluene or isopropanol); as an adhesive for glass and ceramics (in acetone); as a varnish to fix identity markings on historical artifacts (20% in acetone); and with micro-balloons as a filler for stone and other substrates.

iii) on indoor objects deeper impregnation with acrylics can be achieved by multiple applications of very low % of acrylic in suitable solvent mixes that allow the resin to travel into the stone without evaporating too quickly.

Typically for Paraloid B72 on stone 1-2% is used on fine stones in 1:1 solvent mix of acetone and ethanol to prevent discolouration of the stone, allow for better impregnation, and prevent resin interfaces or zoning when resin is deposited too close to the surface.



c) acrylic polymer/alkoxysilane mixtures ('The Bologna Cocktail')

i) Many conservators have experimented with B72 dissolved in an alkoxysilane as the idea is that the acrylic gives adhesive properties that the alkoxysilane lacks.

This treatment was successfully used in San Petronio Cathedral in Bologna, Italy from where its name, the "Bologna cocktail" comes from. It was used on a dense impermeable limestone for 'gluing' flakes and its surfaces are apparently still in good condition

ii) When the Bologna cocktail is used with very porous limestones problems occur as the B72 has a very low impregnation capacity, and forms crusts that lead to severe flaking of the stone. The acrylic part also inhibits the cure of the silane component through its hydrophobicity.

iii) Arguably there is no phase interaction of the B72 with the silane and any consolidation is due more to the adhesive properties of the acrylic polymer.

And recent research on the aging of Bologna cocktail mixtures (Paraloid B72 and Dri Film 104) has shown that the resulting composite gel is weaker than the polymers derived either from neat MTMOS or from a solution of B72 in a nonreactive solvent.

d) epoxy resins

i) Epoxy resins have not been very good for consolidation. They can be viscous, brittle, and yellow with UV – they can be good adhesives in some circumstances, but generally not good consolidants.

ii) However some conservators have had some success with the careful choice of solvent, the means of application, and post-application procedures

iii) Some (cycloaliphatic) epoxy resins (eg. Eurostac EP2101) have successfully been used *in situ* in Italy, such as, in 1985 the deep consolidation under vacuum of large, fissured granite columns (Cavalletti et al. 1985).

More recent work has focused on complex hybrids, such as epoxy-silica materials (Cardiano et al. 2003; Cardiano et al. 2005). However much further research is needed to evaluate these materials.

e) perfluoropolyethers

i) perfluoropolyethers (eg Fomblin, Akeogard) are used as water repellents as they have little or no cohesive effect. They are stable under UV and are theoretically removable as they are soluble in fluorinated solvents.

ii) in the 1990's Fomblin introduced a consolidant version that remained mobile in the stone – its performance declined over time and treated stones suffered losses especially in cold conditions.

f) alkaline earth hydroxides

i) calcium hydroxide

aqueous solutions of calcium hydroxide (limewater) have been used for many centuries to protect and consolidate limestone.

calcium hydroxide in water reacts with atmospheric carbon dioxide to form insoluble calcium carbonate, which may bind particles of calcareous stones together - the solubility of calcium hydroxide is only about 1 gm/L at room temperature, therefore repeated applications are necessary to produce sufficient calcium carbonate to consolidate stone.

Unless very dilute solutions are used, only the calcium hydroxide deposited near the surface of a stone is carbonated, usually at around a depth of 2mm which severely impedes the migration of carbon dioxide through the treated surface to the interior of the stone

NB. Any newly produced calcium carbonate is susceptible to the same deterioration processes as the calcareous stone – so it can react with sulfur dioxide to form calcium sulphate which then degrades as we have seen in the ‘Stone Decay’ lecture notes.

ii) nanolime technique

Recent developments in nano-lime technology

- suspends nano-scale calcium hydroxide particles in alcohol to permit deep penetration into stone
- the use of alcohol instead of water limits carbonation by CO₂ before the particles are deposited in the porous stone and facilitates much higher loadings of lime than is possible with limewater
- potential problems include lime ‘blossoms’ and skins/scaling, although many conservators have reported good results



ii) nanolimes

More successful developments have been in 'nano-lime technology':

- they are suspensions of nano-scale calcium hydroxide particles in alcohol that aid deep penetration into a stone
- the use of alcohol instead of water limits carbonation by CO₂ before the particles are deposited in the porous stone and facilitates much higher loadings of lime than is possible with limewater
- potential problems include lime 'blooms' where the stone surface goes white, and scaling as zones can be created between treated and untreated areas. However, many conservators have reported good results on limestones and marble

iii) barium hydroxides

treatments involving barium hydroxide have been used for the consolidation of decayed limestone - in addition to the formation of barium carbonate,

they are designed to convert calcium sulphate into the relatively insoluble barium sulphate - but researchers have reported they generally had no effect or created problems with scaling as they create a dense impermeable surface layer

h) biomineralisation

i) as we saw earlier the production of oxalic acid, which reacts with a calcareous stone to produce calcium oxalate, is of interest, with ongoing research on different lichens and other organisms that can produce calcium oxalate as a protective coating as its insoluble in acid rain

other research has focussed on the creation of a protective layer of artificial calcium oxalate by the exposure of limestone to ammonium oxalate (although irreversible as a coating).

ii) experiments with different bacteria indicate that bacteria could play a role in CaCO₃ precipitation and that mineral formation is not only an indirect consequence of environmental changes, but produced by the metabolic activity of bacteria

iii) the growth of new calcite crystals inside the pores of limestone has been tested in a biomineralisation process that uses inorganic compounds extracted from the shell of a mollusc (*Mytilus californianus*) to precipitate calcite to strengthen stone (but as yet only in a lab).

Application methods

before full scale application of any consolidant, and bearing in mind the criteria outlined above, the conservator should:

i) test in discrete area or preferably on stone/polychromy of object type and characteristics

ii) use in low concentrations at first for penetration + wet-on-wet bonding and sometimes pre-wetting with solvent carrier before application carried out

iii) importance of solvent carrier in application method for penetration - the more volatile the solvent the more rapidly it evaporates leaving the resin deposited nearer the surface and in danger of creating an impermeable interface and glassing/darkening - some slowly evaporating solvents therefore used including xylene, toluene, ethanol

iv) use of appropriate solvent to clean back excess consolidant from surface - acetone

v) apply with brushes, pipettes, syringes, sprays, by capillary absorption, by pressure/vacuum impregnation, and by total immersion - use as appropriate, following all health + safety advice

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