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Consolidant treatment of Irish sandstone

by

Paul Kissane

Thesis submitted to the University of Dublin, Trinity College, for the
Degree of Doctor of Philosophy

2007

Now upon those hallowed walls,
The ivy clinging,
Proud memories too,
That once it knew,
In sadness bringing.
When at dawn the Mass bells rang,
The faithful calling.
Now on ruined altarstone,
The snow flakes falling.
Yet memories proud will linger here,
Down through the ages,
Of prayerful days,
And ruthless frays,
Through history's pages.

From 'The Old Abbey Garden'
In 'Poetry' By Eamonn Monaghan

Declaration

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Paul Kissane

Paul Kissane
October 2007

Abstract

The objective of this study was to assess the efficiency of consolidant treatments in improving the durability of Irish sandstones. Samples of sandstones relevant to national monuments were characterised, artificially weathered and treated with modified alkoxysilane consolidants.

The mass structure, moisture transfer and mechanical properties of unweathered, weathered and treated samples were compared in order to estimate the variation in properties due to weathering and treatment. These variations were used to evaluate the suitability of the treatments. Further weathering tests were also carried out in order to compare the durability of the treated and untreated samples. Treated samples lost considerably less material than untreated ones.

Consolidant treatments were modified by the addition of solvents and nanoparticles; the former to aid penetration in low porosity samples and reduce film thickness, the latter to increase the gel's elastic modulus, improving cohesion and shrinkage resistance. According to the results of this research, the alkoxysilane consolidants increased the mechanical strength of the sandstones tested and improved their cohesion and durability.

The possible impairment of the stone's breathing ability due to the reduction in porosity caused by consolidant treatment was assessed by comparing mass structure and moisture transfer properties. Capillary absorption and evaporation were both reduced slightly, however the net effect was a reduction in the calculated percentage saturation in the sandstone, which was beneficial.

Surface-substrate interface stresses due to poor penetration were analysed using results from a Finite Element Method stress-depth model. Sandstone of low modulus and strength are at most risk. It was observed that they were most likely to fracture during salt crystallisation cycling.

The presence of fine matrix can improve sandstone's cohesion and the performance of consolidation. Where absent the addition of nanoparticles to consolidants can help this. If excessive volumetric content is used or the contents are poorly mixed this may lead to the blockage of pores near the stone's surface. The modulus increases significantly so rupturing is then liable near the surface during further weathering.

The compatibility of the consolidant treatments with the sandstones was assessed using approximated ratings for the incompatibility criteria based on the data obtained from testing and analysis. Risks associated with low penetration and insolation stresses were shown to be more critical than effects on breathing ability for the sandstones tested.

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Chapter 1:

Introduction

Conservation of Irish sandstone monuments

1 Introduction: Conservation of Irish sandstone monuments

As discussed in the Clonmacnoise Draft Management Plan (DOEHLG 2003), there are several statutory acts that cover the conservation of stone monuments.

- National Monuments Acts 1930-1994
- Planning and Developments Act 2000

These provide measures for the protection of architectural heritage through the Record of Protected Structures and Architectural Conservation Areas

There are also additional International and European Legislation and Agreements which Ireland has signed – the Granada Convention (1985) and the Valletta Convention (1992) commit Ireland to protecting architectural heritage, establishing inventories and providing statutory procedures for their protection.

As a result the Office of Public Works - National Monuments are obliged to carry out routine inspection and maintenance to ensure continued stability of monuments, and conservation works where required. The Clonmacnoise Draft Management Plan and the Clonfert Select Vestry have outlined the need to consolidate certain carved sandstone features against further weathering. Consultation with National Monuments and engineers, architects and technicians working in conservation as part of interim reports during this study raised several practical issues and questions as follows:

- Is there an ideal time at which to consolidate?
- What are the effects of salt decay on consolidants and will salt content influence the consolidation of the stone?
- What is the applicability of the consolidants – are they usable by operators on site?
- What is the worst that could happen?

Historically the success of consolidant treatments in conserving important monuments has been varied. The principal uncertainties are related to the performance of the treated stone after further weathering. Many types of solutions have been applied in a variety of mixtures, and despite much research into their results there are still many doubts about their suitability.

Indiscriminate application of consolidants was found to usually produce disappointing results (Building Research Establishment 1971). In many instances around Europe, blind application of *'magical'* products was performed as part of short-term 'restoration' programmes, and the products were often chosen before the monument had even been inspected. One such former magician warns of the consequences, illustrating the advised measures that are now taken. Conservation and maintenance include planning from start to completion of the project and allow for future protection measures, both passive and active. The significance of proper documentation, information and training are underlined, as are the skills and priorities necessary to conserve today and protect tomorrow (Nardi 1998).

In accordance with the ideals of conservation many parties decree that the consolidating process should be reversible, i.e., removal of the consolidant should be possible if future treatments should require so (Burgess 1990). It is practically impossible to find a consolidant that meets this among so many other demands but it is generally agreed that consolidants, if possible, should not impair future treatments and any incompatibilities ought to be considered prior to application. The compatibility of consolidant products with monumental sandstone may be assessed using compatibility indicators to evaluate their harmfulness (Delgado Rodrigues and Grossi 2007).

A recurring feature in literature regarding the consolidation of stone is not only the depth of research required to ensure appropriate treatment, but also the difficulties in evaluating the effects of treatment, as each scenario proves to be different (Wheeler 2005). The prevalent risk is that of applying a consolidant product that will do more harm than good in the long term. Much work has been, is being and will be carried out to understand the processes involved, however each study unavoidably tends to be specific to local stone-types or monuments.

1.1 Historic background of monuments

This study hopes to facilitate decision-making by providing relevant data on the use of consolidants to conserve the sandstone features of the following monuments:

- Temple McDermot ('The Cathedral'), Clonmacnoise
- Temple Finghin, Clonmacnoise
- Nun's Church, Clonmacnoise
- St. Brendan's Cathedral, Clonfert (in conjunction with Clonfert Select Vestry)
- Cormac's Chapel, Rock of Cashel

The following comprises background information obtained from literature on the history of the monuments including their location, construction and exposure.

1.1.1 Cormac's Chapel

Cormac's Chapel is a Hiberno-Romanesque church that was founded in 1134AD on the Rock of Cashel, the seat of the High Kings of Munster and of Ireland. It comprises the most advanced stone-roofed church in Ireland, containing an impressive vaulted croft, 16' (4.88m) wide and 20' (6.10m) high underneath a high-pitch roof. The apparently corbelled stone is actually a facing of well-wrought sandstone courses supported on an irregular pointed arch made of lightweight calcareous tufa, so the structure is actually quite stable against sagging or buckling. The architecture is also notable in that it encompasses many continental influences, particularly from German ecclesiastical buildings, alongside what are clearly English decorations within a distinctively Irish structure (Leask 1955; Stalley 1981).

Tradition asserts that the chapel is built of sandstone that was quarried at Drumbane, 9 miles to the north, and carried hand to hand to Cashel. It is apparent that there was a change in plans during construction as the chancel is eccentric from the axis of the nave. The chancel archway is not only higher in proportion than width but the whole building has height out of proportion to length (McCraith 1923).

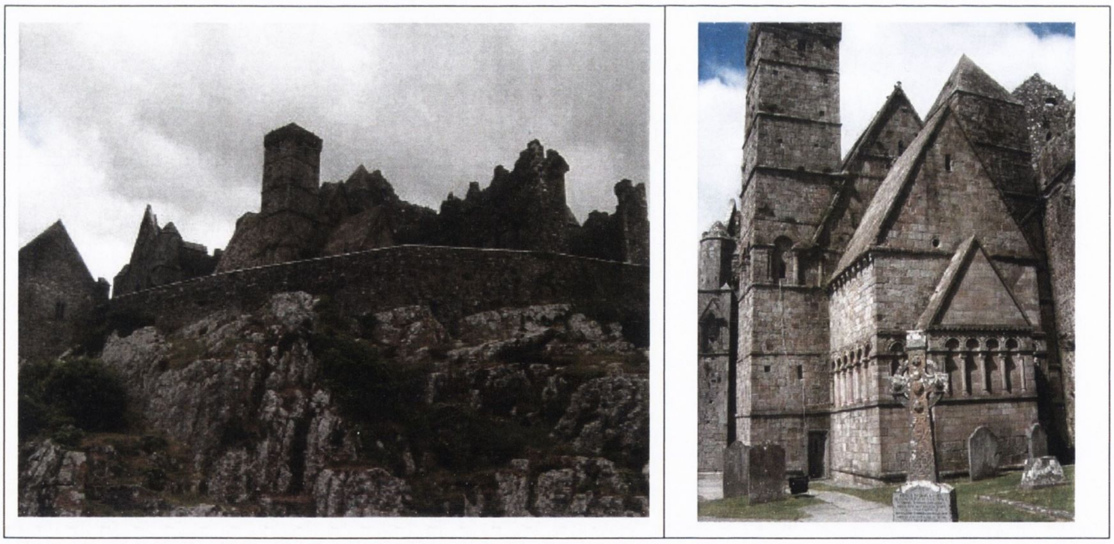


Figure 1-1: Cormac's Chapel on the Rock of Cashel, Co. Tipperary

1.1.2 St. Brendan's Cathedral

The 12th century doorway of St. Brendan's Cathedral is claimed to be *'the triumph of Irish Romanesque'*. Much of the detail is common to all Romanesque phases, with ribbon and zig-zag moulding in the arch rings and chevron-faced voussoirs, among much other ornamentation, and culminating in an amazingly decorative doorway. Again it has much influence from the continent. It is the largest Irish doorway with its steep-sided triangular pediment and has breath-taking beauty and individuality. The doorway contains 7 orders of immense detailing with a variety of mouldings, interlaced ornaments, diverse abaci and a unique arch-ring with voussoirs carved on both the face and the soffit. An inner Gothic door case of blue-grey limestone was added in the 15th century.

On the condition of the stone, Leask notes that it was *'Built entirely of mellow red sandstone which has, of course, suffered, but not so much as might be expected, in the nearly 800 years of exposure to wind and weather which have elapsed since erection.'* Also, the ornamented chevron stones within the doorway were *'sharply carved and quite unweathered.'* (Leask 1955)

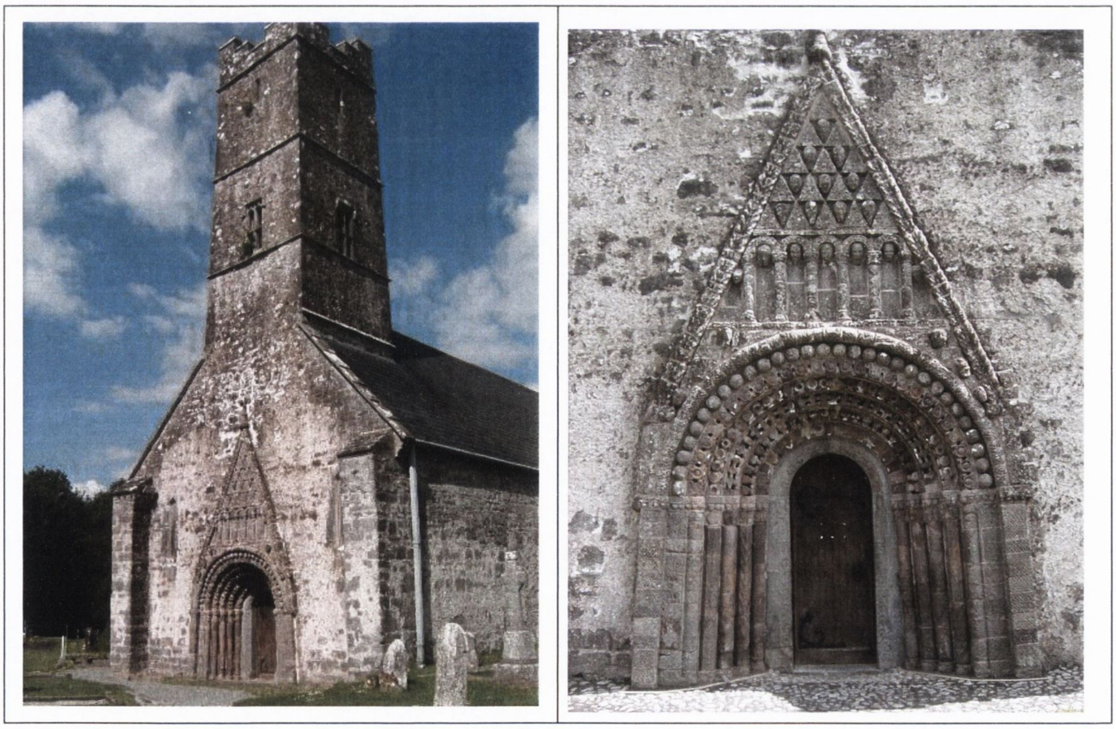


Figure 1-2: St. Brendan's Cathedral, Clonfert, Co. Galway

1.1.3 Clonmacnoise

Clonmacnoise is a heritage site situated on the banks of the River Shannon in the low-lying midlands of Ireland, having once been a busy monastic settlement for over a thousand years from the mid-6th century onwards. Clonmacnoise has been nominated for acceptance as a UNESCO World Heritage Site (Government 2003).

1.1.3.1 The Cathedral

The Cathedral at Clonmacnoise underwent a steady 'architectural evolution' from its foundation in the early 10th century until the late 15th century, and as a result it contains elements of Transitional architecture that developed from the initial Romanesque. The principal features that belie these changes are the south wall, which was reconstructed 2m in from its original location during one of a number of phases of alterations, and the west doorway, made of sandstone, is eccentric from the mid-gable because of this (Manning 1998). As a direct consequence of the nature of some of these renovations the material in structural and decorative elements are now quite varied and difficult to characterise. The building was originally entirely of sandstone, but the south wall was rebuilt using limestone. All repairs and alterations since then have been with a mixture of the two (Manning 1995).

Figure 1-3: The Cathedral, Clonmacnoise, Co. Offaly

Figure 1-4: The Nun's Church and Temple Finghin, Clonmacnoise, Co. Offaly

1.1.3.2 The Nun's Church

The Nun's Church was built in 1166 AD and is a nave and chancel building. The three orders of the arches and west doorway were restored with elaborate detailing. Engaged columns are adorned with double fillets and small bud-like bosses. The capitals are heavy square blocks, covered with small-scale interlacing, key patterns and stylised foliage, indicating that the designer was not a mason. The three orders of the arch and doorways are bounded by hood-moulding with running chevrons, animal masks with open jaws and a plain inner order (Leask 1955).

1.1.3.3 Temple Finghín

Temple Finghín is a small nave and chancel church to which is adjoined by a remarkable round tower belfry. The chancel is small and almost square (8'6" by 8'8" or 2.59m by 2.64m), while the nave is long and narrow (29' by 14'5" or 8.84m by 4.41m – ratio 2:1). The chancel is more complete; however the nave is ruined almost to the ground. The church would have been constructed between 1160 and 1170 AD. There are a few small windows, of which the one in the east of the chancel is round-headed and splays slightly inwards. The chancel arch is less than 6' (or 1.83m) wide and has three orders of jambs and arches. The innermost is later in date, having taken the place of the original. Colonettes, beak carvings, chevrons and simple moulding details feature in the arch. The belfry was built with squared sandstone ashlar straddling the southern junction of nave and chancel. It is 12.5' (3.81m) in diameter at the base, 2.5' (3.05m) less at the eaves (48' above ground level, 14.6m), and the apex is at 56' (17.1m). The roof is corbel built, with each course rhomboidal and opposing, producing a herring bone effect (Leask 1955).

Chapter 2:

Aims and Objectives

2 *Aims and Objectives*

The objective of this thesis is to assess the efficiency of consolidant treatments in improving the durability of Irish sandstones.

To accomplish this, a thorough understanding of the behaviour of consolidants applied to Irish sandstones is required. Therefore partial objectives of the study include:

- To determine the physical properties of the Irish sandstones studied
- To study the weathering behaviour of the sandstones
- To define a standard procedure for the correct impregnation of sandstone with consolidant
- To determine the physical properties of treated sandstones
- To compare the properties of the treated and untreated sandstones in order to assess the efficiency of the consolidants
- To evaluate the durability of both treated and non-treated sandstones

This list may be subdivided under three main headings relating to the characterisation, weathering and treatment of Irish sandstones respectively.

The objectives of the Characterisation are to determine the petrographic features, mass and moisture transfer properties, and the mechanical strength of the Irish sandstones studied. Since the composition and properties are inter-dependent their analysis can be complementary in understanding the current condition and behaviour of the stones.

The objectives of the Weathering testing are to determine the durability and weathering behaviour of the samples. In addition, weathering prepares the samples for consolidant impregnation in order to test the suitability of the treatment.

The objectives of Consolidation are to determine the properties and durability of consolidated sandstones, and to modify tetraethoxysilane (TEOS) treatments using:

- Solvents, to reduce viscosity, enhance penetration and deposit a thinner film

- Particle Modified Consolidants (PMCs), to increase modulus, vary the consolidant properties and reduce the effects of cracking during condensation

Chapter 3:
Literature Review

3 Literature Review

Much literature is available on research investigating the behaviour of consolidants when applied to stone and the resultant change in weathering. To review this literature specifically would probably result in a text similar if not identical to Wheeler, (2005), *'Alkoxysilanes and the consolidation of stone'* (The Getty Conservation Institute, Research in Conservation series). On closer inspection there are dozens of categories into which the studies could be classified; comparisons of treatment types, condition assessments of previous treated surfaces, physical and chemical theory for the mechanisms involved in weathering, models of material interactions, for example.

The literature reviewed here discusses studies that were relevant to the following broad topics:

- Sandstone characteristics, weathering and durability
- Consolidant treatments and effects

3.1 Sandstone characteristics, weathering and durability

There are many studies on the properties of sandstone, especially for durability and for the conservation of buildings and monuments. The underlying principle in all of the studies is the dependence of the properties and weathering of the stone on its composition and exposure. Furthermore, the composition and properties of sandstone contribute directly to the suitability of a sample for consolidant treatment.

The effects of weathering are visible on the surface of the stone, although they also alter the stone substrate underneath. Decay types are distinctive and characteristic of a sandstone sample's intrinsic properties and the weathering environment. The presence of salts and their contribution to weathering of sandstones is covered in more detail, since accelerated weathering by immersion in salt solutions is a common method for evaluating durability and consolidant suitability.

These topics are especially relevant to the understanding of the condition of the case study monuments and also the laboratory work necessary to determine the suitability of the consolidant treatments.

3.1.1 Sandstone composition

The constituent minerals in stone largely determine its resistance to weathering by exposure to the environment, contributing to strength and durability.

By definition the most common component of sandstone is quartz. Quartz is a crystalline form of pure silica (silicon dioxide, SiO_2) that is hard (Moh's scale – 7), is chemically stable and resistant to decay, only dissolving in extreme conditions (Pavía and Bolton 2000). On a molecular level it also has a low thermal expansion coefficient due to the strength of its open oxide structure (Newnham 2005).

Other common constituents include iron oxides and alumina-silicates. Iron oxides generally occur in small amounts in sandstone, but even a small content can cause noticeable colour changes. Haematite (Fe_2O_3) and limonite (Fe_3O_4) are common in sedimentary stones.

Feldspars are alumina-silicates that split easily along their cleavage planes, allowing the ingress of water that can weather the feldspar into micas and clay minerals. Micas are soft, sheet-structured minerals, breaking into sheets along one well defined cleavage plane. In sandstones they are mainly visible when looking onto a horizontal plane. They can also exchange ions during hydration or combination with other minerals. Clay minerals are fine plates and crystals that can also exchange ions, and often promote expansion and contraction with the absorption of water. Sandstone containing clay minerals can have varying degrees of durability; sometimes they are easily eroded while sometimes they provide considerable cohesion and are resistant to weathering (Pavía and Bolton 2000).

A petrographic or thin section description of a sedimentary sample should represent grain composition, texture, matrix, cementation, compaction, replacements, classification, depositional environment, diagenesis and porosity. Of most significance with respect to weathered sandstones are the textural aspects such as grain size, shape, sphericity and roundness. These variables have a strong influence on the pore structure of the sandstone (Tucker 2000).

3.1.2 Sandstone properties

The properties of sandstone most relevant to weathering and consolidation may be looked at under three main headings; mass structure, moisture transfer and mechanical strength.

3.1.2.1 Mass structure

The mass structure of sandstone describes the arrangement of the mineral masses in the material and consequently has significant effects on all other properties and the durability of the stone.

Porosity is the percentage of voids in the stone by volume. The open porosity is the amount of empty space in which moisture or salts may enter. If empty and near the surface this space may allow vaporisation of moisture into the gas phase. Primary porosity is that due to interparticle voids whereas secondary porosity is due to modification processes such as the dissolution of cement minerals. The regions of pore spaces can be defined as being fine, medium or coarse depending on the size of pore throats, nooks or open space, allowing for the packing and cementation that occurs in sedimentary stone (Meng 1992).

Winkler compiled sandstone porosities from previous authors. Sources quoted interparticle porosities of between 25% and 40% for uncemented sandstone and between 15% and 30% for sandstone after lithification. Another source quoted by Winkler evaluated the porosity of sandstones to lie in the range 5% to 25%. Density is the ratio of mass of dry specimen to volume. It is dependent on the packing of the grains and minerals, and has an inverse relationship to porosity. Sandstone densities can be from 2,000 kg/m^3 to 2,600 kg/m^3 (Winkler 1975).

3.1.2.2 Moisture transfer

Water absorption is the measure of the amount of water in pore spaces during immersion. It is closely related to interconnectivity and size of pores and therefore also permeability. Percentage weight increases due to water absorption are in the order of 1%-12% for Irish sandstones. Capillary suction is the movement of water through narrow pores due to surface tension at the interface between the water particles and the pore walls (Addleson and Rice 1994; Pavía and Bolton 2000).

The horizontal transport of liquids through capillary materials is described by the formula:

$$X = (\sigma.r/2\eta)^{1/2}.t^{1/2} = A.t^{1/2} \qquad [1]$$

where X is the displacement of the liquid front, σ is the surface tension of the solution, r is the average capillary radius, η is the viscosity of the liquid, t is the time and A is a constant related to the permeability of the material to the liquid (Munnikendam 1971).

It will be noticeable that since different liquids have different surface tensions their behaviour in capillary movement may also be different. The wetting characteristics of the set of liquids relevant to the study (water, TEOS, MEK, iso-2-propanol, ethanol) will be discussed later in *Chapter 5: Methods and Materials*.

The water absorption of sandstone samples was found to correlate quite well to its surface roughness, although the test seemed to reach a maximum absorption time at a certain roughness, showing little difference when applied to rougher surfaces (Grissom et al. 2000).

New parameters or 'capillary indices' were proposed for use by the Italian Protocol Norma UNI 10859:2000 *'Cultural Heritage-Natural and artificial stones-Determination of water absorption by capillarity'*. A critical survey of their use in determining the effects of treatment products on water absorption outlines the theory and suitability of such parameters in experimental testing (Peruzzi et al. 2003).

Studies proved that the assumption of 1-dimensional imbibition was most accurate for stones of low porosity; however, for samples of higher porosity it is more likely to involve some 3-dimensional behaviour. Petrographic measurements and effective medium statistics were used to relate capillary imbibition and micro-structural characteristics in sedimentary rocks. Allowances were made for 3-D actions, non-circular pore shapes and indirect pore orientations in capillary imbibition described by the Washburn Law and applied to an idealised pore structure with pore throats of regular length and effective radius (Benavente et al. 2002).

Meng (1992, 1993) focused on the relationship between pore characteristics such as pore radius, pore size distributions, pore fraction distributions or fractal dimensions and moisture transport processes, noting that there is good correlation between them and the transport coefficients for diffusivity, permeability, capillary behaviour and the sorption isotherm. Capillary rise is relevant in pores of radius in the range 10^{-7} to 10^{-3} m, while sorption is related to the range 10^{-9} to 10^{-7} m. Permeability is relevant to pores of down to 10^{-8} while diffusion is relevant to all sizes.

The drying process of stone can be divided into two important stages; the first controlled principally by external conditions and the second dependent mainly on the stone macrostructure. Initially the evaporation of liquid from the surface is regulated by the environmental temperature and relative humidity. When the evaporating surface is depleted of liquid and its movement towards the surface is lower, the evaporation is limited by the capillary forces and the pore structure (Colantuono et al. 1993).

The effective size of pores in the pore network is indicative of the absorptive characteristics of the stone. The effect of weathering on pore size distributions was investigated. Comparisons between weathered and fresh samples of very porous calcitic sandstone (open porosity 33-37%) were established by mercury intrusion porosimetry. Recrystallisation of the calcite in the larger pore range enhanced the pore surface area and thus shifted the pore radius distribution to smaller values (Pérez-Bernal and Bello 2000).

The behaviour of the moisture content of natural stone and humidity were correlated, by evaluating the pore surface area, capillary uptake, water saturation, drying behaviour and also equilibrium and disequilibrium sorption. They cited the role of moisture dependent processes in stone decay as the motivation for the study, hoping to provide information that may serve to characterise the materials and aid further research on weathering and conservation (Franzen and Mirwald 2004). They obtained values of approximately:

- 0.89 $kg/m^2/h^{½}$ for capillary absorption coefficient (equivalent to 8.65 $g/m^2/s^{½}$)
- 5.0% for maximum capillary moisture uptake

- 5.6% for moisture content after vacuum saturation

3.1.2.3 Mechanical strength

Weathered stone usually suffers from loss of strength (Pavía and Bolton 2000). Compressive strength is defined as the load per unit area that causes failure of a cube sample. The compressive strength can be measured by crushing cube samples in mechanical apparatus (Perry 1999).

Winkler also reports on the tensile strength of rocks, ascribing it to the strength of mineral grains, cement and the interface area between minerals. This property is pertinent to the resistance of the stone to expansive salt crystallisation or freezing water, and may be determined using the hoop stress test. Tensile strength is normally only one-fifth to one-tenth of the compressive strength (Winkler 1975).

Modulus of elasticity is the relationship between stress and strain of a material as it deforms. The modulus of elasticity (E, GPa) of sandstone can vary in the range 3-80 GPa and is considered to be semi-elastic (Winkler 1975).

Poisson's ratio typically lies within the range 0.15 to 0.35 for sandstone, depending on porosity. This is a measure of the ratio of lateral strain to vertical strain in a stressed material, and is relevant in the determination of the modulus using ultrasonic velocity testing.

The surface hardness of a material is a measure of the strength of the material, tested on the surface. There are several types, ranging from Moh's Scale of Hardness, where materials are tested on a relative scale of 1-10, where talc is 1, steel is 5 and diamond is 10. Another measure is the hammer rebound test that gauges the impact resistance of the surface to a cylindrical mass loaded on a standard spring. With calibration it can be used to determine semi-non-destructively the compressive strength of the material (Chew 2002; West 2003).

3.1.3 Sandstone surfaces

The visual appearance of a sandstone surface is the most obvious measure of the condition of the stone. Given that the effects of weathering and other environmental conditions are initially observed and inspected by visual assessment the appearance of a surface is of key importance. Photo archives and surveys are common in the conservation of buildings and monuments (Leask 1955; Pavía and Bolton 2002).

The colour of sandstone can often betray its principal mineral components. Colour is often quantified as a combination of the logarithmic wavelength of the colour of light and the reflectance, or intensity of the light. The assessment of colour changes due to weathering or treatment is typically measured by chromatic variations in these parameters (Young and Freedman 1995; Garcia-Talegon et al. 1998).

The roughness of a surface is a quantitative measure of the exact surface profile, determined from a datum. It may be represented as a distribution of the distance from the datum to the surface measured at regular intervals in a sample area (Harder 2004). The surface area of sandstone depends on the nature of the pore structure and as a result will change significantly when minerals are lost due to weathering or when pores are lined during treatment.

The surfaces of buildings radiate the energy of the sun through both light and heat forms. The energy absorbed by the surface can cause thermal differential stresses, depending on the modulus of elasticity of the material or differences in the orientation of the minerals. A study by Pombo & Martin demonstrated the differences in thermal radiant energy from stone surfaces due to differences in colour and roughness (Addleson 1972; Pombo Fernandez and Martin 1997).

3.1.4 Weathering and decay processes

The weathering of sandstone has been widely researched and is fairly well understood, although studies find different viewpoints where results are sample specific or where there are underlying assumptions or approximations.

There are many extrinsic and intrinsic factors that combine in the weathering of stone. Extrinsic factors include climatic conditions such as weather and proximity to moisture sources. The severity of exposure of a building surface to weathering elements can be roughly assessed by location and using driving rain index classification (Addleson 1972). The compatibility of environmental conditions in temperate regions may be assessed by rating climatic performance criteria.

Temperature, relative humidity, annual rainfall, wind, sunshine, groundwater conditions and other possible hazards are rated for values between 0 (perfectly compatible) and 10 (highly incompatible). The quadratic mean of all the ratings indicates how severe the environment is to the monument (Delgado Rodrigues and Grossi 2007).

Intrinsic (but non-material) factors such as bedding orientation, placement and size also determine the resistance of the stone to the effects of the exposure (Pavía and Bolton 2000).

Decay is due to the cumulative effects of environmental stresses like wetting and drying episodes, frost action and salt or biological activities. The inheritance of structural and mineralogical weaknesses from previous processes leaves stone vulnerable to these stresses (Warke 1995).

The following sections explain the various processes that take place in stone because of exposure to the environment, outlining the mechanisms by which changes occur and the decay that becomes manifest:

3.1.4.1 Cement minerals and moisture

On initial exposure of sandstone to the atmosphere, the freshly cut surface forms a superficial crust. This is due to evaporation of inherent moisture or 'quarry sap' from the stone, depositing silica from solution near the surface and resulting in a hard, less porous exterior surface and a softer, more porous interior. For this reason monumental sandstone is normally roughly shaped as soon as possible before being left to season so that the bulk of shaping is done before it hardens. The fine detail is carved after this hardening, allowing better craftsmanship (Schaffer 1972; Lazzarini and Tabasso 1989).

Analysis of weathering on soft highly porous and poorly cemented Hastings Bed sandstone found that despite much granular disintegration, the friable unweathered stone developed protective silica crusts. Secondary deposition of silica was seen to have filled pores and covered the outer grains to depths of 150-300μm under SEM inspection. The resultant crust caused by such dissolution and redeposition processes slowed down the rate of weathering (Williams 1997).

The cement minerals in sandstone are more easily attacked by moisture than quartz grains. Silica is effectively insoluble, so its dissolution is very slow, while carbonates are highly soluble, especially where the atmosphere contains sulfurous pollutants (Atkins and Jones, 1999) (Hatch and Rastall 1965; Pavía and Bolton 2000).

Silicates are also gradually weathered by the presence of moisture as ions can hydrate slowly at the surface. H^+ ions can then easily penetrate the minerals due to their small size, breaking up the silicate structure. The breakdown of feldspar to clay structures is a result of this type of process. The proportion of SiO_2 to Al_2O_3 is an indicator of the degree of sound stone, given the proportions present in the fresh stone (Winkler 1975). An older study of silicate weathering rates predicted that to reduce the silica content from 47% to 27% in a temperate climate (250-500mm rain) it would take between 2200 and 4400 years (Strakhov 1967).

The weathering of minerals often results in the loss of constituent molecules or their hydration with moisture, for example. Some of these reactions can cause discolouration of the stone, as in 'iron-bursting' or in mineral dissociation. Sometimes the loss of clay matrix can also reveal underlying minerals and alter the appearance of the stone. The degradation of minerals in aggressive environments is described as being a dynamic, non-linear cyclic process with irreversible results (Winkler 1975).

3.1.4.2 Granular disintegration and differential erosion

The dissolution of cement minerals results in the progressive loss of cohesion between constituent grains. The surface grains of quartz are easily loosened and blown or washed off, resulting in granular disintegration, the principal weathering form to be encountered in monuments. Due to its layered deposition and variable composition sandstone may often contain material of varied durability or strength locally within adjacent strata. The weaker layers are more easily eroded by granular disintegration, resulting in differential relief at the surface (Pavía and Bolton 2000).

A model was proposed for surface dissolution processes in stone decay, given that as chemical interactions take place on grain boundaries and in microcracks, the progression of material losses is controlled by diffusion. Steady state weathering rates were calculated, and surface damage was found to increase with the square root of time, after an initial incubation period (Hoke and Turcotte 2004).

3.1.4.3 Wind effects, flaking, and blistering

Wind passing over irregularities on stone surfaces causes the air particles nearest the stone to accelerate, thus inducing lower air pressure in the area closest to the irregularity. Indeed wind erosion has been shown to effectuate the decay of stone monuments by the detachment of the material particles, brought about by continuous reduction of particle adhesion. For particles to remain attached adhesion forces must counterbalance weight, suction forces and shear forces caused by the impact of airborne particles and direct wind action. The reduced pressure facilitates greater evaporation and through expansion and contraction of the stone leads to alveolar decay. Repeated evaporation of moisture, in combination with dissolution processes or salt content, causes flaking. Stresses near the surface cause the detachment of thin irregularly edged fragments of material from the surface of stone. Blistering is effectively part of the same process and is due to superficial swelling and lifting leading to flaking (Delgado Rodrigues and Gil Saraiva 1985; Quayle 1992; Pavía and Bolton 2000).

3.1.4.4 Scaling and thermal stresses

Scaling is due to the same stresses as flaking, however it results in the detachment of much larger laminar or planar pieces from the surface. Differential thermal stresses and salt crystallisation are more likely to have an influence, generating shear forces in the stone. If stone elements are face bedded this lamination is much more likely (Pavía and Bolton 2000). In the case of sandstone with high clay content showing the effects of contour scaling, the damage done may reach a point after which it is too late to apply treatments of any sort (Wendler et al. 1992). The hygric swelling and shrinking that causes this is less of a problem in Ireland's more humid climate (Scherer 2005, pers. comm.).

Differences in thermal expansion can cause magnified stresses due to large differences in mineral sizes. The temperature differences between inner and outer surfaces are of little relevance to Irish stone buildings (Pavía and Bolton 2000).

Insolation weathering causes the outer surface to be lost due to *'heating of the shell unless overcome by cohesion of materials'*. It was previously proved that *'the most important thermal gradients are reduced to the first few millimetres of rock'*, so in general it is in the minerals at the surface more so than at the surface-subsurface depths where thermal effects have most effect (McGreevy et al. 2000).

3.1.4.5 Fractures and fatigue

Fractures occur in a stone when a stress exceeds the capacity the stone can withstand in a locality, and which may propagate further until the level of stress lowers below the strength of the stone again, similarly to the explanation by Scherer (1999) described in *Section 3.1.5.4* below. These stresses are generally due to salt crystallisation, water absorption or frost action (Schaffer 1972). Rupturing of stone fragments is similar to fracturing, however it refers to the breakdown and separation of more compact pieces and can be caused by structural building failure (Pavía and Bolton 2000).

The stress at a crack tip is locally concentrated, exceeding the tensile strength hence cracks and fractures propagate with each load cycle *'even if the mean stress values in a cross-section are relatively low.' 'Slow and stable crack growth at the interface of the aggregate grains is the most important process which determines fatigue.'* (Brandt 1995)

Standard fatigue strength is generally specified as being the reduced strength after the order of 2 million stress cycles. A few values from a study of the combined effects of fatigue and freezing-thawing cycles allow for a quick comparison later on: after 2 million cycles of loading from 10% to 40% of its initial value, the flexural strength of plain concrete was reduced by 25% and its flexural stiffness by 20%. 300 cycles of freezing and thawing then caused greater deterioration to the outer 6mm. It was proved that the fatigue damage was critical as the levels of micro-cracking were increased when freeze-thaw cycling was carried out first (Forgeron 2004).

3.1.5 Stone durability and salt crystallisation

3.1.5.1 Stone durability

A stone's durability is its resistance to deterioration and weakening by weathering processes. It is difficult to define a simple parameter for this since weathering rates may vary and are a function of composite and complex interactions (Turkington 1995). Warke attributes decay to the cumulative effects of environmental stresses such as wetting and drying cycles, frost action, salt attack and biological activity. Hence durability can be expressed as a combination of the disruptive forces of decay and the cohesive forces of the stone (Warke 1995).

3.1.5.2 Decay due to salt crystallisation

It is where the deposition of salts along a 'drying line' occurs that damage is caused by crystallisation. This occurs when the rate of moisture migration to the surface lags the rate at which the moisture evaporates, resulting in flaking, blistering or spalling in the zone of solute deposition (Lewin 1982). It has also been said that salt decay is a threshold phenomenon so decay is manifest only when a stress/strength threshold is crossed (Warke and Smith 2000). The slow withdrawal of the salts to the surface has been shown to be one process responsible for granular disintegration. Moisture transfer is strongly dependent on pore sizes and connectivity so salts that crystallise in the micropores may easily accumulate to such an extent that they obstruct many pore spaces and inhibit moisture movement, which, as described above can lead to fracturing (Smith and Kennedy 1997).

The resistance of the stone to sodium sulphate and other salts was observed to decrease as the proportion of fine pores increases, causing crumbling and powdering at the surface. The theory behind the migration of salts in solution in pores was illustrated quite effectively with special consideration for practical aspects and unknown variables in salt removal. The amounts removed in subsequent treatments is probably the most straightforward evaluation of the quantity of salt removed (Jedrzejewska 1975).

Hence, stone durability is normally evaluated using salt crystallisation tests to determine the balance between pore characteristics and material strength.

3.1.5.3 Salt crystallisation tests

Salt crystallisation tests comprise repetitive cycles, immersing stone cubes in salt solution and subsequently drying them. The main parameters to be analysed after the test are the percentage weight loss of the sample, changes in porosity characteristics and the final decay conditions (Pavía and Bolton 2000). The change in weight after each cycle is the net change due to the accumulation of salt in the pores and the corresponding decrease by disintegration (Schaffer 1972). Should the stone contain much clay minerals then it will be more susceptible to the accelerated weathering. The salt solution shall disrupt the stone structure further with the salts crystallising from the stone on evaporation of the solvent. Variations include the use of 50mm cubes treated on four sides with consolidant, but left untreated on the bottom and top, whether on natural or vertical bedding. The effects of salt crystallisation are concentrated on the top surface, and it is more appropriate for confirming the visual effects of weathering than for determining mass losses (RILEM 1980).

The crystallisation test methods of RILEM PEM-25 (1980) and BS EN 12370:1999 are most widely used in European studies and can be tailored to cater for durability and treatment efficacy characteristics. The damage caused is not simply due to degree of supersaturation and location, but also depends on environmental conditions and interactions between the salt and the substrate. The importance of the kinetics in the interactions between salt solutions, substrate material and the surrounding environment were noted. Criticism of the standard crystallisation tests report that some believe the test to be too severe and that the results are sometimes inconsistent (Doehne, 2002, 2003).

Sodium sulphate is the most common salt for crystallisation tests, as its hydration is accompanied by a large volume expansion (315%) as thenardite (Na_2SO_4) becomes mirabilite ($Na_2SO_4.10H_2O$).

3.1.5.4 Sodium sulphate crystallisation mechanisms

McMahon *et al* (1992) investigated the deterioration mechanisms of sodium sulphate crystallisation by controlling environmental conditions such as using partial or total immersion, encouraging evaporation or by changing temperature. Five mechanisms were tested on concrete samples of varying strength and porosity:

1) Rapid crystallisation of mirabilite ($Na_2SO_4.10H_2O$)
2) Crystallisation of mirabilite due to evaporation
3) Crystallisation of mirabilite due to combined evaporation and temperature changes
4) Crystallisation of thenardite (Na_2SO_4) due to evaporation and hydration
5) Crystallisation of thenardite due to evaporation

The first mechanism was the most severe resulting in complete destruction of samples, with decreasing amounts of damage due to mechanisms three and four, while mechanisms two and five lead to slight mass increases with little or no damage. The crystallisation pressures cause the pressure of the solution to rise, displacing it through the pore system, and where this flow cannot proceed in sufficient time the material may crack. The fourth mechanism is that which occurs in the standard salt crystallisation tests such as ASTM C88, BS EN and RILEM PEM-25. The second one utilises partial immersion of the samples to promote the crystallisation of mirabilite near the exposed surface (McMahon et al. 1992).

The chemistry and thermodynamics of crystallisation have been studied in depth (Charola and Weber 1992; Scherer 1999; Rodriguez-Navarro et al. 2000). Scherer explains that the pore size, the chemical potential of the solution and the interfacial energy between the pore wall and the crystal determine the level of stress experienced in the pore walls of the material. As the crystals grow due to supersaturation they may propagate through the pore network, and fractures will only result if sufficiently high stress is exerted on an area containing a strength limiting flaw. Mirabilite can crystallise around the edges of thenardite crystals if a saturated solution is allowed to evaporate, whereas in a steady environment no growth or dissolution occurs. With continued evaporation both the mirabilite and thenardite precipitate, with the mirabilite dissolving and precipitating as thenardite. This process is slow, with only partial hydration after 5 hours. Below 63% relative humidity, mirabilite will dehydrate (Scherer 1999).

Flatt builds on this thermodynamic reasoning. Experimental measurements of the stresses generated due to mechanisms including those of thenardite dissolution, evaporation and the growth of flaws indicated that the stresses were of the order of 17-20 MPa, although these values should be approximately halved in the case of cylindrical pores. The salts crystallize preferentially in larger pores, where chemical potential is lower. Eventually salts crystallize in the smaller pores, generating higher pressures. In some pore structures this is found to cause surface hardening of the stone rather than disintegration, with an even higher proportion of fine pores, as the larger ones are already filled with salts. Consequently even higher stresses are possible, causing exfoliation and crumbling of the crust (Flatt 2002).

3.1.5.5 Comparison of accelerated weathering tests and decay in monuments

Environmental and visual conditions were related to durability tests, charting the progress of salt decay in materials. The results were used to predict and hence tailor inspections, and the link between the qualitative and quantitative methods were shown to be reliable (Lubelli et al. 2000).

The inaccuracies of studying single surfaces were highlighted by a study of the distribution of salts within sandstone blocks found in deteriorated buildings. The relationship between the salts at the surface and the concentrations in the inner material was found to be quite complex, so the study concluded that extrapolating from artificial salt weathering data may not be reliable (Turkington and Smith 2000).

3.2 Consolidant treatments and effects

Many years have passed since consolidants were first used so there is much literature available on the different types of consolidant products, the development of consolidants and their application to various types of substrate.

The science and theory of adhesion was comprehensively covered in the 1984 Paris Congress entitled 'Adhesives and Consolidants'. In the application of liquid adhesives the available molecular forces of attraction and repulsion combine with elements of the surface roughness and the wetting properties of the liquid to fulfil their purpose. The applied liquid must spread over the surface and then change phase, solidifying to provide the required strength of adhesion (Allen 1984). Similar processes are involved in the application of consolidants, and although the fields of adhesives and consolidants have become quite distant since then, it is still these actions of physicochemical adsorption that bond a consolidant to stone surfaces.

It was at the same time that the ability of 25 different stone consolidants to strengthen crushed granules of sandstone and limestone was measured. Some of the tested consolidants were deemed to have failed because the treated samples did not withstand any force, which was a reasonable conclusion (Price 1984). Certain products are not suitable for bridging gaps between particles of that size encountered in this test. It is worth noting just how many products were available then though. There is a wide range of consolidant products available for application to sandstone. These include epoxies, vinyls, acrylates, polyurethanes, perfluoropolyethers, fluosilicates, alkoxysilanes and siloxanes (Young et al. 2003).

Consolidant compositions have changed quite often, and choosing a consolidant treatment is generally a very specific task, requiring knowledge of the substrate and the product's characteristics. It is often emphasised just how important it is that the mineralogical composition, petrography and pore characteristics be properly analysed before any work is carried out with consolidant products (Lazzarini and Tabasso 1989; Nardi 1998; Pavía and Bolton 2000).

A suitable consolidant has several qualities:

1. To ensure sufficient penetration while liquid it should be have low viscosity, low-moderate surface tension and sufficient gelation time

2. To ensure improved cohesion and mechanical strength it should have good adhesion to the stone's constituent minerals and its elastic modulus should not be too low

3. To ensure durability it should be physically and chemically compatible with water and salts

4. So as not to inhibit the evaporation of moisture from the stone it should have film-forming abilities

5. To avoid problems with stresses at and below the surface its elastic modulus should not be excessively high

Alkoxysilanes satisfy most of these requirements. Tetraethoxysilane (TEOS) and Methyltrimethoxysilane (MTMOS, an alkyl-alkoxysilane) are two of the more common alkoxysilanes. MTMOS is similar in structure to TEOS but with methyl content that alters the properties slightly, adding some water repellency at the expense of some consolidating power (Ashurst and Dimes 1990).

Alkoxysilanes have been and still are worthy of much research focus (Wheeler 2005). The remainder of this review will focus on TEOS, or other alkoxysilane treatments, but will refer to other product types if relevant.

3.2.1 Gelation of alkoxysilane consolidants by hydrolysis and condensation (the sol-gel process)

Before and during application, alkoxysilanes are liquid polymers in which the molecular structure incorporates principally methyl (CH_3–) or ethyl (C_2H_5–) radicals around a central silicon atom by oxygen bonding. They undergo the sol-gel process, hydrolysing and condensing until all carbon is converted to alcohol and emitted. This results in a silica xerogel, effectively a gel film that lines the pore system. The principal difference between the various alkyl and alkoxy arrangements is the rates at which hydrolysis, condensation and gelation proceed, although they do affect viscosity and other liquid properties. Of course these ultimately affect the bonding of the consolidant to the substrate and the thickness of the film deposited in the pores, among other characteristics (Lewin and Wheeler 1985; Honeyborne et al. 1990; Wheeler 2005).

The hydrolysis of an alkoxysilane requires a catalyst and the presence of moisture to proceed. In the case of pure alkoxysilanes this necessitates minute additions of water and either an acid or a base to start off the process. Commercial products are pre-hydrolysed in order to ensure that local environmental conditions do not inhibit this first step of the sol-gel process however (Goins 1995). These same products are generally catalysed with a heavy metal ingredient like 'stannane' (dibutyltindilaurate, DBTDL), thus overcoming the need to follow the more sensitive acid or base catalysis reactions. Furthermore these reactions can lead to different gel products. During the condensation process, the hydrolysed alkoxysilane monomers and oligomers combine to form larger polymers, increasing the degree of polymerisation. The solvent by-product separates from the gel ('syneresis') forming the gel networks of silica and increasing in stiffness, eventually causing cracking. This condensation reaction continues by repeated combination of available silane oligomers until no more are available to combine, due to either a lack of moisture or to isolation of these in the gel. The strength and stability of the resulting siloxane bond is often applauded as being on a par with low viscosity as TEOS's most desirable property (Wheeler 2005).

In assessing the condensation of hydrolysed TEOS to silica it is noted that the rate of structural evolution and of evaporation of ethanol are most important in determining the amount of shrinkage and cracking. Hence the catalyst type and content can have a significant impact on the development of cracking during curing. Initially the meniscus is at the exterior and evaporation proceeds at a constant rate until the gel network is stiff enough to withstand pressure. The rate of evaporation then drops and the meniscus retreats further into the substrate body. The gel is then attempting to shrink while its structure is progressively becoming more and more resistant to shrinkage, so stresses inevitably keep increasing. Since the gel network has a low permeability the tension is greatest near the drying surface (Scherer and Wheeler 1997). If this surface shrinks much faster than the interior, differential strains develop which then cause warping and cracking, thus slower drying can sometimes be better (Scherer 1988). The pore sizes of gels were also measured using an innovative beam-bending experiment and bulk solution-gel specimens prepared from TEOS. By modelling the viscoelastic response to bending, the permeability of the gel was hence determined due to the imposed pressure gradient. From this the average pore diameters were calculated to be approximately 6.5nm in during gelation (Scherer and Wheeler 1997). As a result of this it can be seen that both the pores and the gel are shrinking, so stresses increase steadily because the properties to withstand them are changing; area is decreasing, while modulus is increasing. Linear shrinkage of a sol-gel when evaporation is not reduced is approximately 50%. This is accompanied by an increase of about three orders of magnitude in the shear modulus of the gel, much more than the doubling that occurs when evaporation is prevented (Scherer 1989).

3.2.2 Gelation in alkoxysilanes applied to sandstone

Goins (1995) explored the effects of substrate pH on the resultant silica film and found that xerogels formed in acidic sandstone samples bonded better to the substrate than those in alkaline limestone samples by reason of the silanol bonding. This is the nature of silicate sol-gels, whose polymerisation is fully dependent on the pH conditions. Slow hydrolysis occurs in the presence of carbonates, but this is overcome in commercial products like Wacker BS H100/Wacker BS OH100 (Wacker Chemie) and Tegovakon V100H/Tegovakon V100OH (Degussa Gmbh) that are pre-hydrolysed and contain catalyst components. The poor film formation seen in carbonates reflects the difference between adsorption or physical attachment to sandstone substrates and simple shrinkage to cover the pore walls, as with limestone substrates.

Consequently weathered sandstone is most susceptible to changes in surface acidity due to environmental conditions. Hydration of the quartz surface may cause acidic-basic interactions to take place at the surface, which can in turn affect the ability of the consolidant to bond directly to the hydroxyl ions. Catalysed commercial products steer somewhat around this problem; however it is still of relevance to the bonding of the gel to the stone (Goins 1995).

Alkoxysilane bonding is not capable of bridging gaps of more than approximately 50µm. Wheeler (2005) refers to Nishiura (1984) who found that alkoxysilanes were not suitable for *'granularly decayed stone.'* Further reference is made to Wendler (1999), who showed that the corresponding maximum grain size which may be consolidated is approximately 325µm. Hence where granular disintegration, flaking or scaling is present and the particles are greater than this size, the gels are unlikely to provide considerable consolidating action as the area of bonding would be insufficient.

The presence of salt concentrations and biological growth can also result in weak particulate gels. These problems should be primarily considered in regard to their effects on moisture within the stone. Bacteria and fungi pose little threat due to their poor attachment to surfaces. Algae and lichens do retain much moisture at the surface and can be removed using either water or increasingly solvent rich water/solvent mixtures and light mechanical action. There can be a risk of staining from some species however. Also, consolidants can only reduce damage due to further salt crystallisation. (Wheeler 2005)

3.2.3 Consolidant application and modification

3.2.3.1 Preconsolidation

Preconsolidation is a superficial consolidant treatment applied in order to facilitate cleaning that would otherwise cause *'considerable irreversible loss of stone,'* where *'surface conditions such as scaling, flaking, exfoliation, or severe granular disintegration exist.'* Fragments of loose stone may be bonded to the monument by sealing along the fracture with consolidant using a syringe. This may need to be carried out before complete consolidation of a monument although it will probably impede impregnation of later applications. Adhesive polymers may be required for this, and some common ones, such as acrylic resins and polyvinyl alcohols (PVA) can actually be dissolved by certain MTMOS treatments, however they are only sparingly soluble in TEOS solutions and in OH100 treatments they are essentially insoluble (Wheeler 2005).

3.2.3.2 Application techniques

In summarising the techniques and conditions for applying alkoxysilane products, Wheeler highlights most of the practical problems and solutions. Natural-bristle brushes are best for applying consolidants to small objects as they allow excellent control without introducing air bubbles and limiting evaporation. Runoff, and hence waste, is minimised as the amount applied at any time is reduced. Other apparatus that are common include; pump sprayers, mist sprayers, squeeze bottles and pipettes, but these all have certain drawbacks. Application should be continued until a sufficient depth of penetration has been attained, based on porosity calculations. Any excess must be removed from the stone or a glossy surface can result. The rates of application achievable are typically 0.3 m^2/h (DegussaGmbh 2004; Wacker 2004; Wheeler 2005).

3.2.3.3 Application and gelation conditions

The environmental conditions should be within the range of 10°C, 40% relative humidity (RH) and 32°C, 80% RH, and the surface to be treated should be dry. Tenting or awnings should be used to block out direct sunlight and reduce the rate of evaporation. If the relative humidity is too low then excessive evaporation may occur before gelation, shear deformation may occur before cracking, while in humid conditions the skin of the gel can wrinkle. At 20°C and 50% relative humidity the majority of the gelation process should be completed within 2 weeks; however the process may not be fully finished until 4 weeks have passed. Surfaces may show slight beading before curing is complete, however this does not mean they are hydrophobic (Caddock and Hull 2002; DegussaGmbh 2004; Wheeler 2005).

3.2.3.4 Modification by the addition of solvents

In the past, solvents have been employed to either promote penetration or to dilute the treatment and avoid ‘over-consolidation’ (Wheeler 2005). Using a solvent normally not only further reduces the viscosity but also ensures that the consolidant treatment is sufficiently dispersed and thus spreads more evenly in the substrate pore system. The deposited consolidant concentration decreases with penetration due to the migration of solvent during curing (Burgess 1990). The interactions between solvents, polymers and substrates and the resultant effects on the effectiveness of consolidant treatments were previously investigated. Solvents such as acetone, 2-butanone, isopropanol and ethanol have been used in alkoxysilane consolidants in the past (Wheeler, 2005). 2-butanone, known also as methyl-ethyl-ketone (MEK), is a dipolar aprotic solvent that is slightly basic, which means that it does not have acidic hydrogen available, unlike protic solvents such as ethanol, which may dissociate H^+ ions. Ethanol is an alcohol with polar amphiprotic characteristics. Isopropanol is a tetrahedral secondary alcohol and has polar amphiprotic characteristics (Marcus 1998).

Stronger solid-polymer composites are achieved when the interactions are less acidic or less basic, and the bonding of the polymers to the substrates occurs where there is *'an exothermic, interfacial, acid-base reaction'*. A neutral solvent is deemed best in order to maximise the polymer-substrate interactions in a *'triangle of interactions.'* (Goins 1995)

A comparison of the resulting consolidant deposited on the sandstone substrate was investigated by Zarraga *et al* (2002). They noted that MEK was a better solvent for TEOS than ethanol because the polar nature of ethanol makes the treatment product less compatible with the sandstone surface. Investigation by NMR and SEM showed that a solution of TEOS+ethanol resulted in a thick and brittle film, whereas a solution of TEOS+MEK resulted in a thin and continuous film. It was also observed that the TEOS+MEK solution had a higher degree of polymerisation in its structure. They confirm that this is due to a better chemical affinity between the sandstone and the TEOS+MEK solution. The better consolidant efficacy of the MEK over the ethanol solution can be attributed to the chemical properties of the solvents. It was concluded that the ethanol, TEOS and sandstone substrate formed a *'competitive acid-base triangle'* that leads to the development of cyclic trimer rings in the structure, rather than contributing to an orthogonal silica structure (Zarraga et al. 2002).

3.2.3.5 Modification by the addition of nanoparticles

The preparation of thin films by sol-gel processes has for a long-time been using nanoparticles or colloidal oxide minerals to reduce gel shrinkage as well as improve stiffness, thermal and optical properties. As a result they can be help to reduce cracking and tailor the properties in a gel (Etienne et al. 1998; Yang et al. 1998).

The sizes of the particles used in Particle Modified Consolidants (PMCs) have varied from 10nm to 350nm from a variety of sources. PMCs have used fumed silica (Aerosil OX-50, particle size approximately 40nm, surface area $50m^2/g$) and Stöber monospheres (350nm diameter). Even at low contents, the Aerosil particles added significantly to the viscosity of the solution. The maximum volumetric content that could be added was 25%. Viscosity was seen to increase greatly if the ratio of larger particle to smaller particle content was greater than 9:1. The viscosities were 2.4 mPa.s and 2.8 mPa.s, for their SiO_2-PMC and Al_2O_3-PMC respectively (Yang et al. 1998; Escalante et al. 2000; Aggelakopoulou et al. 2002; Miliani et al. 2003).

Escalante *et al* (2000) examined the addition of iron, colbalt, chrome and titanium oxides to act as pigments and alter the thermal expansion coefficients of the gels. By mixing the composition of the PMC to suit it is possible to vary the stiffness, optical reflectance and thermal expansion as required. For particle loadings greater than 10% by volume, the permeability of the gels is high. The samples that contained silica attained the highest modulus of elasticity when applied to stone samples and these suffered least weight loss during salt immersion durability tests. They had a *'flat appearance'* rather than glossy.

Xerogels containing SiO_2:Al_2O_3 content were found to have varying levels of microporosity. Complete silica content resulted in high microporosity and homogeneous structure, while the opposite was true in the case of complete alumina content (Bandosz et al. 1998). 10-20 nm particles of silica were used to coat larger oxide particles thus acting as a steric dispersant and preventing agglomeration. Ultrasonic preparations also helped to avoid the agglomeration of the particles, using ethanol and isopropanol as solvents (Aggelakopoulou et al. 2002).

Miliani *et al* (2003) successfully applied PMCs of titania, alumina and silica to sandstone, using of silica for steric stabilisation. Total nanoparticle content was between 26-29% by volume while the solvent content was approximately half. It was demonstrated that different properties of density, strength, optical reflectance and thermal expansion were achievable by varying the nanoparticle contents. There was an increase in the elastic modulus of the film (105% and 30%) and a reduction in its thermal expansion (36 and 30%) due to the presence of the particles, so ultimately the consolidant film was more durable. The inclusion of the particles increased the consolidants viscosity and therefore impeded its penetration however.

3.2.3.6 Aggregation and agglomeration of nanoparticles

According to Ke and Stroeve (2005) *'particle dispersion is one of the most urgent problems to be addressed'* in polymer and silica nanocomposites.

A lack of control due to the speed at which aggregation (the joining together of individual particles to form larger flocculations or agglomerations) occurs is the main microstructural problem in particulate gels (Wyss et al. 2005). The problems of aggregation were noted in each of the studies mentioned in the previous section. For example Yang *et al* (1998) claimed that Stöber particles did not affect solution viscosity but were large enough to settle, while Escalante *et al* (2000) noticed heavy agglomeration of oxide nanoparticles in PMCs.

The aggregation of nanoparticles dispersed in a solution occurs by a combination of three mechanisms; by perikinetic aggregation, by orthokinetic aggregation and by differential settling. The first is due to Brownian motion collisions, when *'the concentration of single, primary unaggregated particles exceeds that of any other individual aggregate type'*. The second is due to fluid motion, since mixing or stirring increases the number of particle collisions. When particles aggregate, the larger flocs begin to settle and these then fall from solution and hit smaller particles on their descent, providing the third mechanism (Gregory 2004). This is another mechanism by which the aggregation and phase separation of nanoparticles occurs which is explained by the physics of volume exclusions. All polymers, their monomeric precursors and solvents interact by excluded volume repulsions and Van der Waals attractions (Graessley 2004). Depletion forces result from such volume exclusions, forcing the larger particles to aggregate where there are two sizes of particles present (Helden et al. 2006).

3.2.4 Consolidant-sandstone systems

Up until now this half of the literature review has covered the consolidant products and how they work, the use of additions and their effects on the gels, but the most important aspect is yet to be addressed: what are the effects of the treatment and how is the performance of consolidant-sandstone systems assessed?

The lining of the pore system by the consolidant film is supposed to improve strength and cohesion between its constituents. Moisture transfer may also be changed or thermal differential stresses induced in the stone in and around the zone of penetration. These changes are referred to in greater detail throughout the remainder of this section.

3.2.4.1 Failure and success of consolidant treatments in conserving sandstone

Most failures arising out of consolidant application to surfaces are due to inadequate penetration of the treatment into the stone. If the penetration is too low, it can result in poor attachment of the surface to the substrate and in some cases form a hard outer surface. Unsuccessful treatments have been seen to lead to increased decay on limestone monuments because the surfaces blistered due to dilation of a superficial layer causing further cracking and resulting in scaling. *'Decohesion'* of the grains under the superficial layer was due to the consolidant only poorly penetrating into the stone and then forming a stiffer surface with different thermal behaviour to the underlying stone (Fassina and Borsella 1993).

Finite-Element Methods (FEM) have been employed in the past to determine the effects of consolidation on insolation stresses due to heat expansion of the treated surface. Ratios of modulus of elasticity of treated and weathered stone around the layer interfaces were used to calculate the stresses between the two layers. The danger of such damage occurring was thought to be greater where the geometry of the substrate is complex such as in intricate carvings (Hosek and Panek 1985; Bossert et al. 2004).

Despite being more chemically compatible with sandstones an 18-year review of 54 monuments treated with Brethane^{TM} (the Building Research Establishment, (BRE)'s alkoxysilane consolidant), showed statistically that this consolidant performed better on limestone. This was thought to be as a result of the higher porosity of the limestone samples, which facilitated better penetration. It was observed that the outer 1mm of the stone surface proceeded to weather at the same rate after treatment, and that the underlying stone and polymer remained untouched. This leads to the possibility of surface maintenance with hybrid products, as re-treatment to depth would not be required again (Martin et al. 2002). Overall the use of this product was found not to have caused any long term damage to stone, rather it reduced the rate of decay, extending its life and enhancing its character and appearance. The product is no longer available (Fidler 2002). It also demonstrated that catalyst content avoids some of the problems of alkoxysilane bonding to carbonates.

Munnikendam (1973) cites poor penetration of the consolidant and retraction of the consolidant by the evaporating solvent as reasons for crust formation on the stone surface, which was the most frequent cause of failure in treated samples. The surface crust blocks the pores, thereby inhibiting moisture transfer across the surface and trapping moisture inside the stone where it can induce stresses through salt, dissolution or freezing processes.

Several studies concluded that Wacker BS OH100 had better penetrating ability than other silicate consolidants, however it was felt that it gave low cohesive strength and could by improved by mixture with an acrylic (Nishiura et al. 1984). Tegovakon V100OH was found to be the most effective of a range of consolidant and protective treatments for sandstones in Spanish cathedrals, stating that *'water absorption is controlled in some cases by the consolidant.'* (Valdeon et al. 1992)

As pointed out by Wheeler (2005), application of the product should be continued until a sufficient depth has been achieved, based on simple porosity and volume calculations. The resistance to acid of treated stone samples was previously determined, as were the effects of the treatments on the appearance of the stone and the thermal expansion properties (Price 1984). He recommended penetration of 25mm as being characteristic of a good consolidant; however he does refer to an earlier proposition that it be the depth at which all incoherent material is solidified and attached to the sound core of the stone (Torraca 1976).

The issue of retreatment of consolidated stone was addressed by Nandiwada & Price who investigated the effect of multiple applications of several MTMOS- and TEOS-based products on stone (Nandiwada and Price 1995). Ageing experiments were carried out on the samples as soon as they had attained constant weight after the treatment. Problems encountered during the study arose for many reasons:

1) The solvent employed caused swelling of the stone during the first treatment
2) Pores blocked by the first treatment prevented penetration by the second treatment
3) The second process disrupted some of the bonding between the first treatment and the stone
4) Interference effects hampered polymerisation of the second treatment
5) Biological attack occurred after the second treatment

3.2.4.2 Testing: Studies, parameters and measurements

There have been hundreds of individual case studies on stone types, exposure conditions, weathering forms and consolidant treatments used. Laboratory testing often gives a representative measure of the success a treatment may have, and tests can be tailored to characterise the most relevant parameters. The comparison of untreated and treated sample porosities is easily done, and is often given as an indicator of the effect of the treatment.

Mosquera *et al* (2002) characterised the pore distribution of treated stone using mercury porosimetry. They discovered that the pressure of the mercury caused the gels to shrink, as the intrusion was accompanied by a reduction in pore volume.

A study on the use of porosity and other physical properties as criteria for establishing the effectiveness of consolidant treatments concluded that ethyl silicate solutions reduced pore diameters and that only the smallest pores were affected significantly (Garcia Pascua et al. 1995).

More than the characterisation of the porosity is required to gauge the durability of the material however, whether treated or untreated. Porosity attributes have strong influences on both capillary absorption and evaporation behaviour, which are important for weathering processes. These and other moisture transfer properties are responsible for the majority of decay effects in stone (Price 1980).

Using over 200 cold-curing polymer systems on samples of German sandstone, the effects of treatment on moisture transfer properties were experimentally determined. The products used included polyurethane, epoxy and acrylic resins, polysiloxanes and modified silica esters among others. Capillary absorption, evaporation, drying velocity, water suction, water vapour diffusion and water vapour adsorption were all reduced by the treatments. Only some of them had hydrophobic qualities. Inspection of pore structures treated with epoxy resins by SEM, which was found to be a *'most effective technique'* revealed that polymer microlayers of nano and up to micrometer dimensions were formed lining the pore system with a *'supporting corset'* and sealing up *'only the micropores.'* (Honsinger and Sasse 1990)

This ideal arrangement is shown in Figure 3-1:

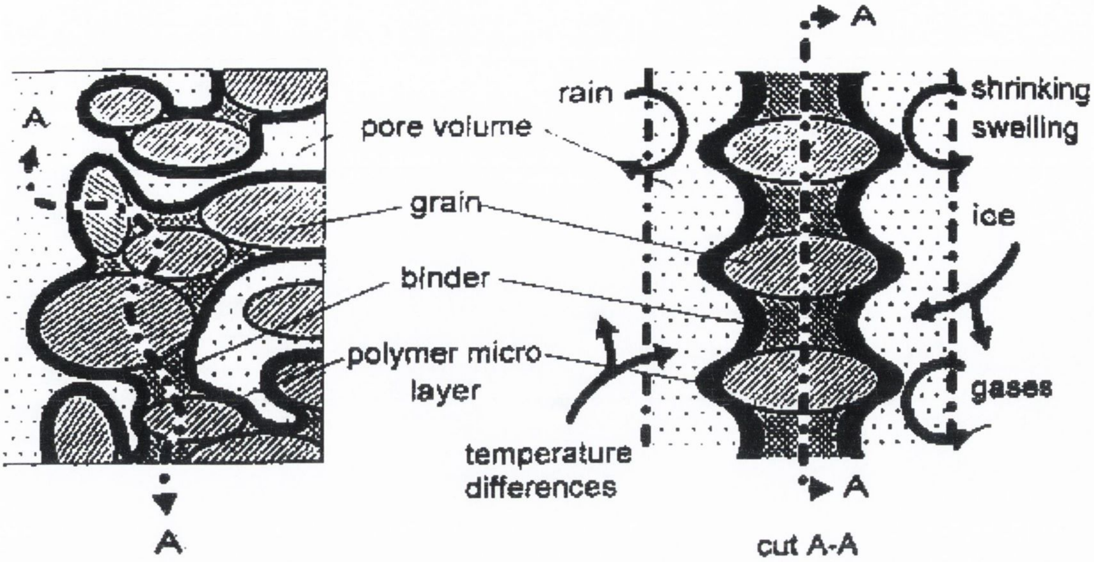


Figure 3-1: Arrangement of polymer microlayer around pore space (from Honsinger & Sasse, 1990)

Sandstones treated with consolidants or water repellents were found to restrict the penetration of salts after alkaline, acid and water cleaning. Soluble salt concentrations were mostly undetected in uncleaned samples. However, after cleaning their soluble ion concentrations were significantly elevated in non-treated samples. The treated samples had much lower overall concentrations with high retention of salts in the outer layers (0-2mm) and none past 5mm depth (Young and Cordiner 1998).

3.2.4.3 The depth of penetration

An important criterion that is difficult to measure accurately is the depth of penetration, which quantifies the depth to which a protective treatment has had an effect. There are several different approaches and techniques for the measurement of the depth of penetration. A combination of direct and indirect detection and assessment methods (including drilling resistance, microdrop absorption, wetting surface behaviour, dithizone staining, acid etching and ultrasonic tracing) is best. The effectiveness for different lithotypes was ascertained in several laboratories, finding that no one method suits all types. The method of staining with dithizone was favoured, however this relies on colour changes and is not reliable for stones containing iron and other metallic minerals. This echoes previous findings that complementary techniques are necessary in order to determine the depths of penetration. (Delgado Rodrigues and Costa 1994; Leroux et al. 2000; Casadio and Toniolo 2004).

The methods involving visual assessment and water droplet absorption rates were discussed further and applied to a large sample group with some success by Young *et al* (2003). The water drop absorption method, adapted from RILEM PEM-25, was employed and was deemed to be valuable but hard to carry out when undertaking many tests, due to the level of variation in placing small drops on a rough stone surface. Again it was shown to be of low accuracy but it was a simple and somewhat effective method.

Changes in moisture transfer properties were used elsewhere to evaluate consolidant penetration (Henriques 1992; Auras 1993). Visual assessment methods were also utilised on sections of stone cut perpendicular to the application surface (Clifton 1984).

A wide range of analytical spectroscopic and microscopic techniques such as IR, Fourier-Transform Infra-Red (FTIR), X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were employed to successfully quantify the depth of penetration on cut cross sections of treated samples (Littmann et al. 1993).

Nuclear magnetic resonance (NMR) was also used to detect and profile the molecular structure of the polymers within the stone. Micro-attenuated total reflection was found to be a worthy technique, assuming in the analysis that the polymer dose at the top surface was 100% and following a characteristic absorption band for the polymer treatment (Casadio and Toniolo 2004).

The resistance of consolidant treated stone to microdrilling has also been successfully used to analyse the depth of penetration of consolidant treatments and even the depth at which decay effects are present. A 5mm drill-bit is employed in controlled conditions for which a graph of force vs. depth is plotted. Changes in force are observed at the interfaces between zones of different strength (Delgado Rodrigues et al. 2002).

3.2.4.4 Strength or durability as the critical indicator

Many studies have used strength parameters to measure the efficacy of consolidant treatments. It has been shown that mechanical testing of samples in laboratory tests provides information on the upper limit of what is attainable under field conditions (Wheeler 2005).

Consolidants of ethyl silicate, acrylic polymers and aqueous dispersions of silica nanoparticles were tested separately on Greek and Cypriot biocalcareous stones and then subjected to salt weathering. Analysis of mass changes, ultrasonic velocity measurements and visual analysis of surfaces showed that the products with higher ethyl silicate content worked best. While the others did manage to prevent some of the salt accumulation they allowed the salts to accumulate at the same rate as in the untreated samples (Cardell et al. 2000).

Relative and absolute changes of shear strength, tensile strength, peel strength, compressive strength, modulus of elasticity and adhesive bonding should be studied in tandem (Bradley 1984). Measurements of Young's modulus by ultrasonic velocity (using PUNDIT apparatus) provide data on the strength of samples, so differences between untreated and treated samples are attributed to the extra strength provided by the consolidant film lining the pore walls (Aggelakopoulou et al. 2002).

This was also determined after cycles of freeze-thaw testing where it was found that stone treated with methyltriethoxysilane (MTEOS) lost only 4% while the untreated stone lost 67%. The water repellency provided by the treatment impeded the absorption of water so the damage due to freezing is much reduced. Acrylic and epoxy resins were also tested but the samples did not endure the freeze-thaw cycling (Nishiura et al. 1984). In artificial ageing, losses can sometimes occur after only a few cycles, eliminating the protection provided by the treatment. The issue of durability and strength improvement was addressed: a treatment that is more durable is more desirable than one that causes the greatest increase in strength (Goins 1995).

3.2.5 Service life and field assessments

As regards the effective service life of treatments it is very hard to predict as each success seems to vary according to individual monument conditions (Wheeler 2005). Practical and simple yet effective methods were used by Nwaubani and Dumbelton (2001) in order to evaluate the service life of consolidant products applied to historic surfaces. The condition of the surfaces was determined by measuring the moisture content and timing the absorption of moisture into the surfaces. The study provided qualitative results and hence required careful interpretation, but was useful for forming opinions on both the condition of past surface treatments and the need for retreatment.

The surveys of the Brethane treated stones estimated the number of years of decay on both treated and untreated surfaces. The extent and severity of granular disintegration, scaling, general decay and water-repellency of the surfaces were assessed and compared. All of the treated sandstone or siliceous stones were in better condition than the untreated ones after periods of between 13 and 20 years (Martin et al. 2002).

These studies were later referred to in a review of alkoxysilane consolidants and their effects on stone durability; stone in relatively good condition at time of treatment will probably remain in relatively good condition, while stone in poor condition will degrade quickly whether treated or not, and if the sources of deterioration are not dealt with the treatment will probably not perform well (Wheeler 2005).

Studies in American National Parks found that original composition, stone condition and the extent to which the causes of decay can be removed determined the success of the treatment. Of note was the failure of consolidants to protect soft granular sandstone for even a few years because the grains had become too loose for the consolidation to work effectively (Oliver 2002). Other case studies reported mixed performance from previous experiments with alkoxysilane consolidants on sandstone. A positive effect was observed in approximately 22% of cases, slowing the decay process, while none altered the appearance of the decayed stone (Honeyborne et al. 1990).

3.2.6 Compatibility and planning of consolidant application

It is obvious from the all of the literature reviewed thus far that the application of consolidants requires planning and care as it can trigger irreversible damage. Guidelines for quantifying the compatibility of treatments with the masonry to be conserved have been defined and demonstrated to be most useful in evaluating treatment suitability.

For example, the following material and substrate criteria can be assessed; chemical and mineralogical composition, pore space, visual properties, thermal properties, mechanical properties, hydrophilic behaviour. Where deemed perfectly compatible, they are rated equal to zero, and conversely where deemed fully incompatible they are rated equal to ten. Some may be decided to be of critical importance, while others may simply be complementary. Their weighting can thus be altered as appropriate. The Incompatibility Degree (ID) is then calculated as the quadratic mean of all the indicator ratings, so for ID = 0 treatment is fully compatible, whereas for ID = 10 treatment is fully incompatible. The method of calculation is such that the output will be quite high if more than one or two factors are incompatible.

This leads to the formation of a checklist, necessitating the consideration of all of the relevant criteria. The assigned ratings readily highlight the factors that require most attention. In this way it is a useful tool to translate laboratory findings and pertinent risks to managers, conservators, engineers, surveyors and whoever else may be involved.

Consideration can also be applied to other criteria types such as operational management, environmental conditions and social and cultural factors. It was highlighted that compatibility should be held *'a step downstream to effectiveness'*, assuming performance guarantees within acceptable limits: *'intervention... must be as durable as possible.'* (Delgado Rodrigues and Grossi 2007)

Chapter 4:
Fieldwork

4 Fieldwork

The prime motivation for this study is to promote the safe and efficient application of consolidant treatments to national monuments in order to conserve them from the exposure they endure. Without investigating the condition, orientation and layout of the monuments, laboratory testing may provide incomparable or inadvisable information.

Factors such as material type and variation, size and shape of individual sections, their orientation to sunlight, and weathering features are important in the consolidation of stone since it is highly reliant and subsequent to surface processes.

The sites studied are monuments containing sandstone features that the OPW wish to conserve using consolidant treatments, as mentioned in *Chapter 1* (DOEHLG 2003).

4.1 Environmental exposure of monuments

The severity of exposure of the monuments may be roughly assessed by evaluating the compatibility of environmental surroundings with the monuments, as mentioned in *Section 3.1.4* and later in *Chapter 12*.

In Ireland there is high atmospheric humidity due to the winds that blow off the Atlantic Ocean and other seas, frequently bringing rain. Humidity is generally greater than 80% RH, but it does go as low as 65%. Average annual rainfall varies between 800mm and 2800mm. The prevailing wind direction is from the southwest, so most rainfall occurs on the western regions. Average daily temperatures are approximately 9°C, ranging from a mean minimum daily winter temperature of 2.5°C to a mean maximum daily summer temperature of 19°C. Ireland receives much less than 2000hours of sunshine annually (MetÉireann 2006).

4.2 Condition assessments

The monuments were inspected in a methodical manner, focussing on the carvings requiring treatment. Recent weather conditions were noted, as were the orientation and location of the structures. Differences between their surface environments were noted and photographs of important details were taken. Variations in colour, bedding, texture and drainage were recorded to help understand the weathering processes.

4.2.1 Cormac's Chapel

The driving rain exposure for the area surrounding the Rock of Cashel is moderate, but due to its elevated site, the chapel should be classified as being severely exposed to driving rain. Parts of the building are exposed to direct sunlight.

The sandstone shows strong weathering due to the severe exposure. The west and south walls have become more highly eroded than the east walls because of the prevailing south-westerly wind. Differential erosion is evident between the grey and rusty sandstone varieties. Differences are noticeable from block to block and also within their depth, as shown in Figure 4-1 (1). Granular disintegration of the surfaces has led to a loss of sharpness in the carvings and walls (4). The weathering is exacerbated by an incorrect orientation of the blocks against their natural bedding (3), highlighting the layered appearance of the weathered surfaces and arcadia restored with fresh stone (2). Biological growth is well established in the sheltered areas of the east wall and doorway. The accumulation of moisture has caused extensive blistering and flaking (6). The stone carvings are less deteriorated than on the west side because of the greater shelter (5).

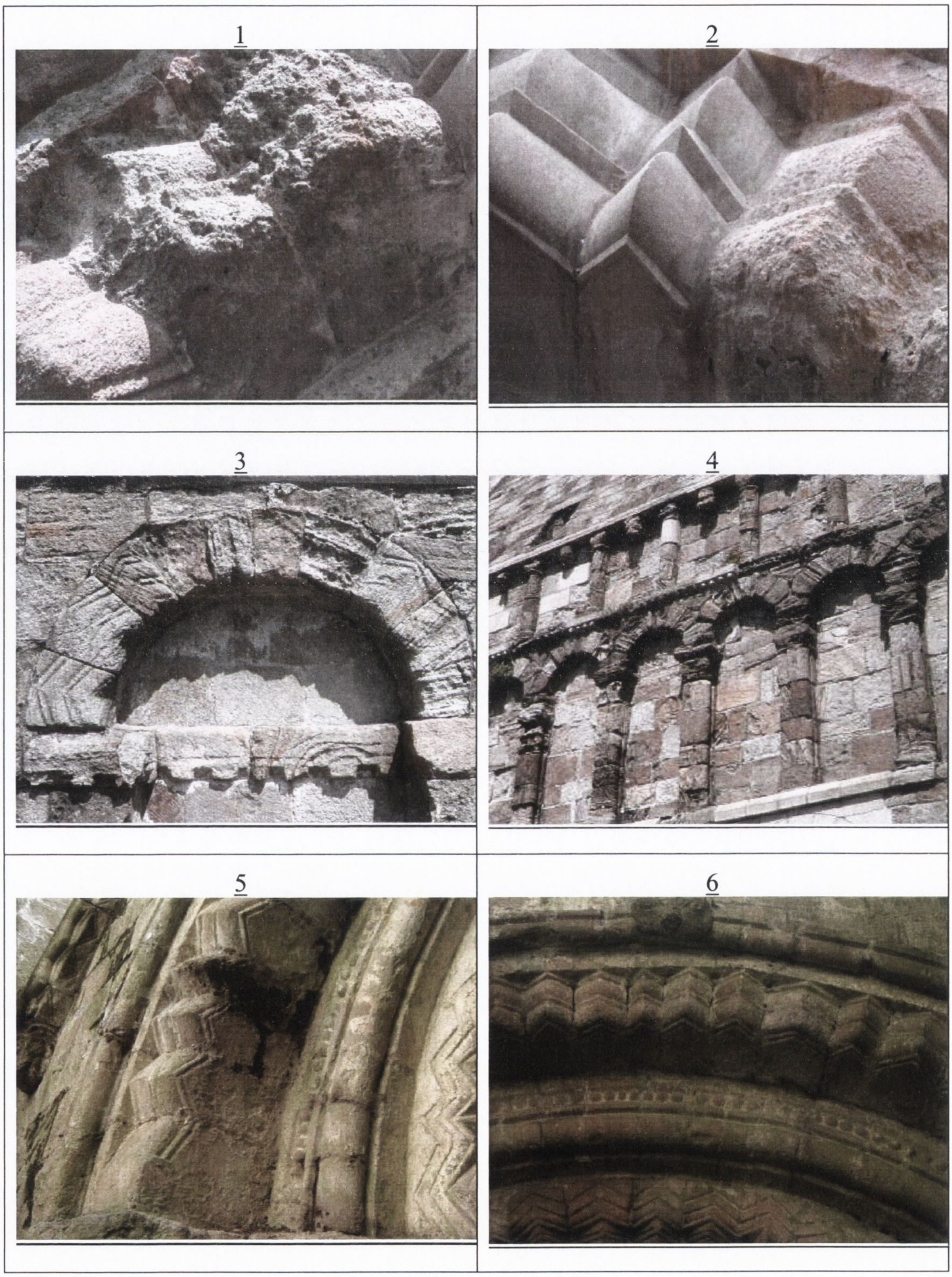


Figure 4-1: Weathering at Cormac's Chapel, Rock of Cashel

4.2.2 St. Brendan's Cathedral

The sandstone doorway faces due west and is in a sheltered location in an area of moderate driving rain exposure. The doorway is situated approximately 35m from the boundary wall which is surrounded by tall trees. It is in close proximity to groundwater and is exposed to direct exposure to sunlight.

At some stage since construction salts have been introduced into the stone in the west doorway. Salt decay has subsequently weakened cementitious matter and dislodged quartz grains, leaving the carved detail highly eroded. Salts have accumulated on the surface of the walls, especially in the joints above the pinnacle of the door moulding, as shown in Figure 4-2 (1). The masonry has recently been repointed (3,4). It appears from the condition assessment that differences in the sandstone's composition have influenced weathering (2). The variation of ferric iron and occasional feldspar content of the sandstone is evident in the shades of buff, brown and ochre. The decay is enhanced at low levels due to capillary moisture because of improper paving materials that have been removed (5,6). Lichen colonisation is also apparent in places.

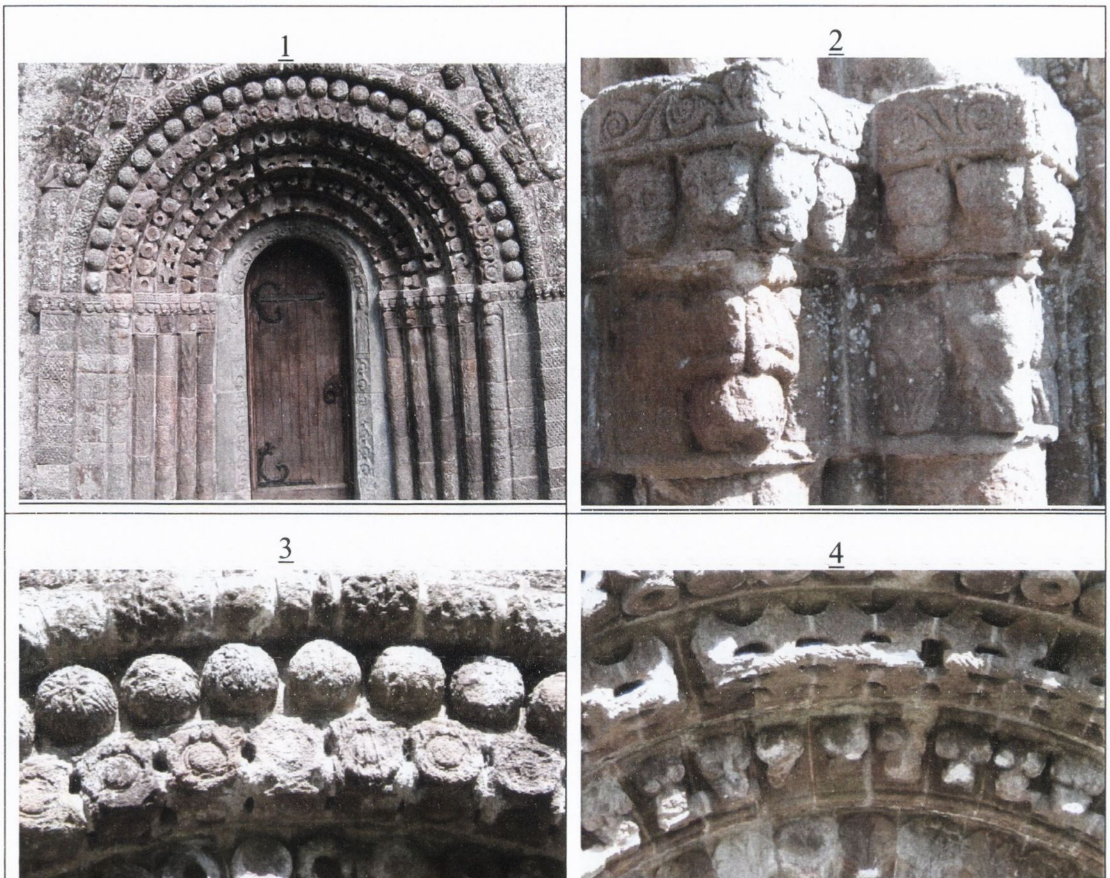


Figure 4-2: Weathering at west doorway of St. Brendan's Cathedral, Clonfert

4.2.3 Clonmacnoise

Clonmacnoise is situated in a semi-elevated location on the banks of the River Shannon. This is an area of moderate driving rain exposure. Parts of the monuments receive direct exposure to sunshine.

The sandstone in the monuments at Clonmacnoise is weathering slowly, and results in a loss of sharpness as seen in Figure 4-3. The weathering is mainly due to rain and wind erosion.

The carvings in Temple Finghin have lost detail due to differential erosion and fracturing (1). The structure has been damaged, with stresses causing the voussoirs to crack and rupture, and ultimately deteriorating the arches even further (2).

The carvings in the Nun's Church have lost their sharpness due to granular disintegration, although it retains most of their character (3,4). Biological growth is evident in the masonry.

The weathering of the carvings in the doorway of the Cathedral has been eroded to a similar condition. The detailing is not as intricate or extensive as in the other monuments (5,6).

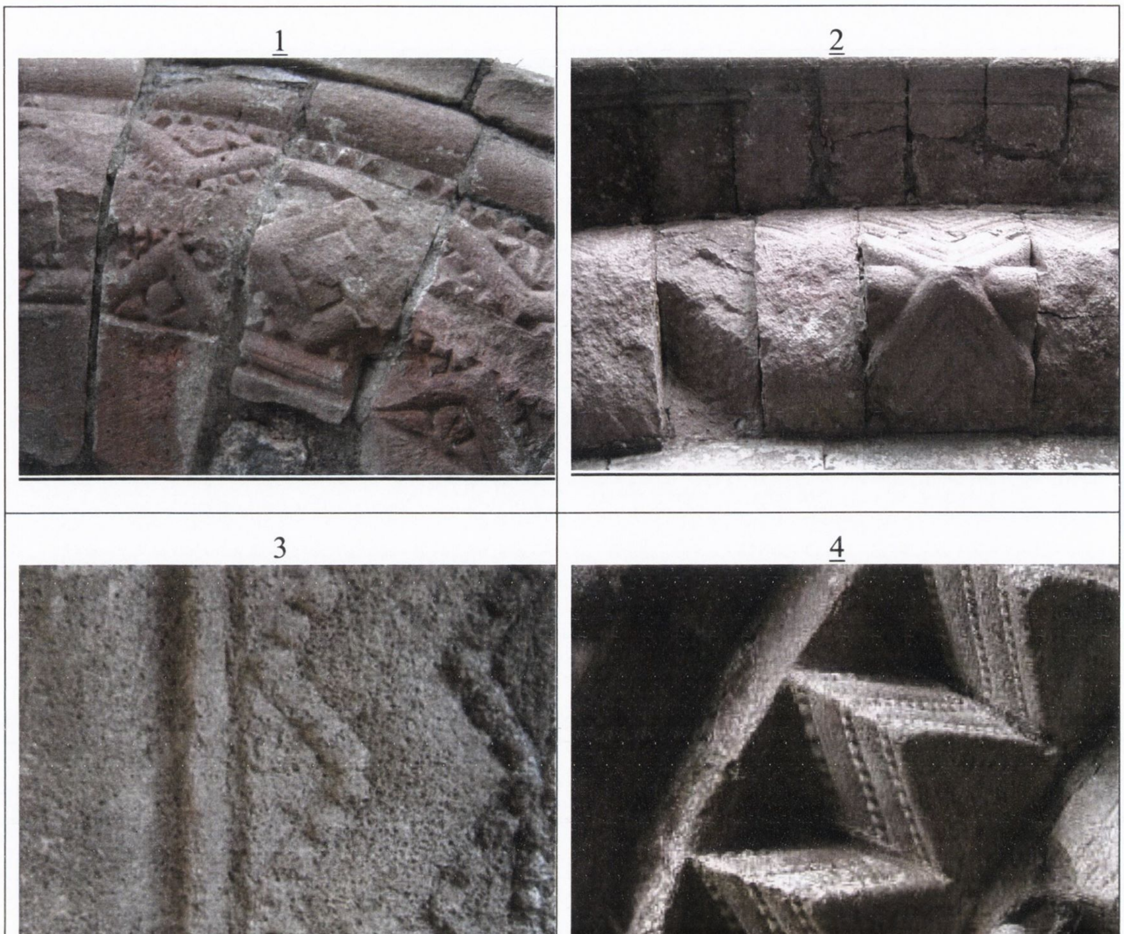


Figure 4-3: Weathering at monuments in Clonmacnoise, Co. Offaly

Chapter 5:

Methods and Materials

5 *Materials and Methods*

5.1 Sandstone sampling

Samples of sandstones relevant to national monuments were provided by the Office of Public Works (OPW) for laboratory testing and analysis of consolidant treatments, including:

- Drumbane sandstone, from Co. Tipperary, was used in Cormac's Chapel, Rock of Cashel. Samples were taken from Cormac's Chapel during restoration carried out by the OPW in 2001. Prisms 100*45*30mm in size were also used.
- A study by Pavía and Bolton (2002) proposed Killaloe sandstone as being similar in texture, colour and composition to the stone in St. Brendan's Cathedral, Clonfert and also in monuments at Clonmacnoise. The samples were held by the OPW, and had previously been sourced from a river bed in the Killaloe area of Co. Clare.
- Clara Hill sandstone, from a quarry near Clara in Co. Offaly, was used in monuments at Clonmacnoise
- Samples of sandstone sourced from a quarry in Manorhamilton, Co. Leitrim, were chosen for possible use in repair works in selected monuments by the OPW.

They were all in the possession of the Office of Public Works at their depots in Kilkenny and Athenry. The majority had been sitting in these locations for less than 5 years. Almost all samples were cut into 50±5mm cubes using a diamond edge saw (the exception being a number of prisms cut from the Drumbane sample). Hence some samples had one or more faces that were slightly weathered.

The test methods used on the samples are outlined in the following sections. Examples of the measurements taken and methods of calculation are presented in Appendix 5.

5.2 Assessment of sandstone composition and properties

The effects of both weathering and treatment on sandstone are measured by changes in its durability, which in turn is dependent on its composition and properties, as shown in the relationships in Figure 5-1 below. These are best captured by the information shown for each, and are dealt with in *Sections 5.2.2* and *5.2.3* on the following pages.

The samples were tested according to the relevant BS/EN and RILEM recommendations, although minor changes were made to some of the standard methods to suit the apparatus available, data required and testing schedule.

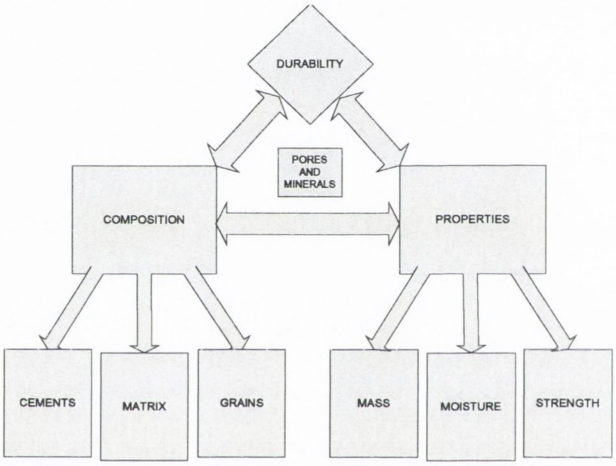


Figure 5-1: Relationships between durability, composition and properties

5.2.1 Petrographic examination of composition

Samples were assessed visually and also with a Nikon polarising microscope. Their colour and fracturing or other weathering characteristics were noted. Thin sections were obtained and studied under both natural and polarised light to analyse the mineral content and texture, according to BS EN 12407:2000 '*Natural stone test methods. Petrographic examination'* at magnifications of 2x, 20x and 40x. The mineral fabric, porosity and secondary mineral alteration were noted as shown in Table 5-1. Estimates of the content of the minerals and pores were made using charts of relative percentage by volume.

Examination of:			Attribute noted:	
Visual	Colour		Variation	
	Weathering		Alteration	
			Fractures	
Petrographic	Minerals	Cements	Type	Quantity
				Distribution
		Grains		Size
				Shape
	Pores		Size	
			Shape	
			Distribution	

Table 5-1: Petrographic assessment of sample composition

5.2.2 Laboratory testing of physical properties

Physical properties were tested in the laboratory to classify the sandstones according to the three broad categories of mass structure, moisture transfer and mechanical strength, as shown in Table 5-2:

Physical property:	Parameter measured:
Mass structure	Mass
	Apparent density
	Open porosity
Moisture transfer	Capillary absorption
	Evaporation
Mechanical strength	Surface hardness
	Compressive strength
	Modulus of elasticity

Table 5-2: Physical properties and parameters measured by laboratory testing

These properties were considered sufficient to characterise the samples and to allow accurate quantification of property changes brought about in subsequent testing investigating weathering and consolidant treatment. These tests were carried out on the samples a total of three times: initially on the unweathered samples, and again after both weathering and treatment, allowing comparison to be made between them.

5.2.2.1 Density, porosity, capillary absorption and evaporation

The mass structure properties of apparent density and open porosity were determined in accordance with BS EN 1936:1999 '*Natural stone test methods. Determination of real density and apparent density and of total and open porosity'*. This method was intertwined with methods for determining the evaporation curves and the water absorption by capillarity in accordance with RILEM Commission 25-PEM Protection et Érosion des Monuments (1980) '*Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods'*, Test No's. II.5 and II.6.

The dimensions of all twelve edges were measured to ±0.1mm using a callipers. The sample group was dried in an oven at 105°C for 24 hours. After cooling for between 2hrs to 3hrs the dry mass of each cube was measured to an accuracy of 0.1g, m_d. They were then placed in a covered tray containing approximately 2mm depth of water and the capillary absorption was measured by taking readings of time and mass, t_i & M_i. Both orientations parallel and perpendicular to bedding were tested within the samples groups.

When the maximum had been reached the cubes were then immersed under water in a pressure vacuum for at least 24hrs. The hydrostatic and surface saturated masses were then measured, m_h & m_s; the cubes were wrapped on 5 sides with cling film and left to dry, mass readings were taken to measure evaporation with time, t_i & M_i. Readings were taken at 15mins, 30mins, 1hr, 3hrs, 8hrs, 24hrs and 48hrs. M_o is the initial reading. Calculations were made using the following equations:

[1] Apparent density, $\rho_b = m_d/(m_s - m_h)*\rho_w$ (kg/m$^{3)}$

[2] Open porosity, $p_o = (m_s - m_d)/(m_s - m_h)*100$ (%)

[3] Percentage saturation, $S = (m_w / \rho_w) / v_p *100$ (%)

[4] Evaporation rate, $q(t) = m / t$, $m = M_w / area$, $M_w = M_o - M_i$ ($g/m^2/hr$)

[5] Capillary absorption rate, $C_{exp}(t) = m / t^{\frac{1}{2}}$, $m = M_w / area$, ($g/m^2/s^{\frac{1}{2}}$)

where $M_w = M_o - M_i$, and *area* is calculated using the relevant dimensions.

5.2.2.2 Surface hardness, compressive strength & modulus of elasticity

Surface hardness measurements were taken on the samples using a Schmidt hammer; usually a non-destructive technique providing information on strength without requiring crushing. The samples were placed flat, resting uniformly on a covered concrete floor. The rebound from the sample surface gives a reading comparable to the compressive strength, when calibrated according to the manufacturer's instruction manual (ELE), s_{surf}. The impact caused some cubes to fracture due to inherent planes of weakness. When this occurred the hardness measurements were not carried out on cubes of similar condition.

The compressive strength of the samples was determined according to BS EN 1926:1999 '*Natural stone test methods. Determination of compressive strength.*' Strain gauges were attached to the faces of the cubes using an epoxy resin. This meant that the cubes could not be placed in an oven as specified in the standard method, so they were placed in a dessicator instead. The crushing was monitored using a System 5000 workstation connected to the strain gauges, and to a 100kN load cell, thus measuring displacement, load and strain to give values for:

[1] Compressive strength = maximum stress at failure, $s_{max} = P_{max}/A$ (N/mm^2)

Data for stress, strain and displacement were also obtained during loading, allowing calculation of the modulus of elasticity.

[2] Modulus of elasticity = Stress/Strain: $E = s / e$ (GPa)

The modulus of elasticity was also determined non-destructively using the PUNDIT ultrasonic velocity apparatus. It required the application of grease between the samples and the transmitter/receiving transducers so was only suitable for use in later stages of tests, as the presence of grease would not be easy to remove and would affect the accuracy of testing to determine mass structure and moisture transfer properties.

The pulse velocity, V, of sound through the samples was measured in km/sec using the PUNDIT apparatus, which was then used to determine the modulus given values for density, ρ:

[3] Modulus of elasticity, $E = V^2 . \rho$ (GPa)

5.3 Artificial weathering of samples

The accelerated weathering tests prescribed in RILEM PEM-25 (1980) and BS EN 12370:1999 were modified in order to induce the principal weathering of a single face on each cube, which could later be treated with consolidants. The samples were artificially weathered by repeated partial immersions in saturated salt solutions, encouraging salt crystallisation at the surface, as described in *Section 3.1.5.4*. They were placed in a container that was then filled up with a 14% solution of sodium sulphate decahydrate to just below the level of the top surfaces of the samples (within 2-3mm). After 2 hours immersed in the solutions the samples were removed from the solution and transferred to an oven set at 105°C. After 21 hours they were removed, and left to cool to room temperature for an hour, or longer if necessary, before repeating the cycle.

After 15 cycles of the artificial weathering the samples were gradually washed free of salts by repeatedly washing and drying in the lab and by immersing in a tank with constantly refreshed water. Washing of salts like this is a difficult process, given that it *'is often the salt that transports the liquid' (*Scherer 1999). Occasionally the samples were left out in open air, so that evaporation of the moisture would bring more salts out to the surface. Mass measurements were taken at irregular intervals during the washing process. No efforts were made to prevent particles getting washed off, yet at the same time no actions were intentionally made so as to encourage the loss of material during washing. Measurements were also taken of the conductivity of the solutions to monitor the estimated concentrations of salt present. The extent of the affected areas was recorded by taking photographs of the weathered samples.

5.4 Consolidant treatments

5.4.1 Comparison of commercial consolidant products used

TEOS consolidant products were chosen for testing because they are compatible with sandstone. This is primarily due to the nature of siloxane bonding, which is dependent on acidic surfaces or neutral surfaces, as discussed in *Section 3.2.1-2*. They form a thin gel film so they conform to the pore walls and are less likely to block pores as a result. They have long been available commercially and may be applied without any modification. These commercial products have been sufficiently developed and have also been the subject of much research.

Tegovakon V100OH and Wacker BS OH100 are two solvent-free TEOS monomer-oligomer blends that are commonly available and have been previously characterised. The principal difference between the two is the degree of polymerisation of TEOS, which affects the viscosity and reaction kinetics. Wacker OH (50% TEOS) is more highly polymerised than Tegovakon V (25% TEOS). The gelation times of Wacker OH and Tegovakon V are 24-48 hours and 15-24 hours respectively. They are both hydrolysed ethyl silicate solutions, and as a result atmospheric moisture does not limit the progress of the reactions. The resultant gels were low in porosity and each had a high bulk modulus. The capillary pressures during evaporation were confirmed to be high in both of the gels, affecting the pore size distributions in the gels. Although both resultant gels have an average pore diameter of 1nm, Tegovakon V has a wider distribution with pores up to 3.5nm compared to Wacker's maximum of 1.5nm (Brus and Kotlik 1996; Mosquera et al. 2003). Research has also looked into the suitability of certain solvents and modification with particles to modify the deposited gel properties, as discussed in *Section 3.2.3*.

They are both susceptible to crack because of syneresis, as discussed in *Section 3.2.1*, so it was important to see what parameters could prevent or minimise their cracking. Their contents and viscosity are shown in Table 5-3:

Product	Manufacturer	% TEOS	Silicate content	Dynamic viscosity	Catalyst content
Wacker SILRES BS 100 OH	Wacker	<50%	~100%	1.6 mPa.s	0.25 % <
Tegovakon V100 OH	Goldschmidt	>25%	~98.5%	3-4.5 mPa.s	1 % <,< 2.5 %

Table 5-3: Summary of properties and composition of consolidants tested

5.4.2 Solvents for use with consolidant products

The properties of the solvents used are presented in Table 5-4 below, and were discussed previously in *Section 3.2.3.4*. Methyl-ethyl-ketone (MEK, also known as 2-butanone), and isopropanol (also known as 2-propanol) were obtained for to modify the two consolidant products. MEK was used in the consolidant treatments applied to the samples. It has a dipolar aprotic nature. Isopropanol was also used in the preparation of gel plates. It has polar characteristics. Ethanol is a solvent by-product of the condensation process and also has polar characteristics (Marcus 1998).

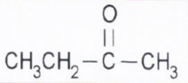
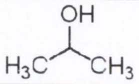
Solvent	Structure (www.sigma-aldrich.com)	Molar mass (g/mol)	Density (g/ml)	Surface tension (mN/m)	Viscosity (mPa.s)	Vapour pressure (kPa)	Dipole moment (D)
MEK	 $CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3$	72.11	0.805	23.7	0.378	12.6	2.76
Isopropanol		60.10	0.785	21.2	2.044	6.03	1.66
Ethanol	CH_3CH_2OH	46.07	0.789	21.9	1.200	7.89	1.69

Table 5-4: Properties of solvents used (MEK and isopropanol) and of solvent by-product (ethanol)

5.4.3 Nanoparticles for PMCs

To design a PMC or any other nanocomposite physical parameters, space distribution parameters and volume fractions should be taken into account (Ke and Stroeve 2005).

Nanoparticles of silica and alumina were obtained from Sigma Aldrich (2004). Their characteristic properties are shown in Table 5-5. Generally nanoparticle silica of diameter 10 nm has a specific surface area of 640 m^2/g, 48% surface hydroxyl, >85% reflectivity of UV light, loose density of > 0.15 g/cm^3 and is an amorphous white loose powder (Ke and Stroeve 2005).

The SiO_2 and Al_2O_3 nanoparticles were added to TEOS in MEK, in amounts of approximately 20% and 5% by volume respectively. Although aggregation would be high for this mixture, the gel would be more permeable and stronger, as found by Escalante *et al* and mentioned in *Section 3.2.3.5*. As a consequence the treatment would perhaps be more durable. Alternatively, while probably not being the worst-case scenario of PMC application, it did allow the scope for treatment failure to be evaluated, whether due to blockages in pores or due to differential stresses between the outer surface and the substrate. This topic is discussed further in *Section 9.1*.

Nanoparticle	Particle diameter (nm)	Specific surface area range (m^2/g)	Particle pH range	Loose density (g/cm^3)	% Surface hydroxyl
Silica	10	590-690	3.6-4.3	>0.15	48%
Alumina	44	35-43	9.4-10.4	-	-

Table 5-5: Characteristics of nanoparticles used (silica and alumina)

5.4.4 Preparation and observation of gel plates

Gel plates were made to study the gelation of the modified consolidants and compare their behaviour. Gel plates were formed from the consolidants (Wacker, 'W', and Tegovakon, 'T') with various combinations of the solvents (MEK, 'M', and Isopropanol, 'I') and nanoparticles (silica and alumina, 'P') to observe any differences between them. The following gel plate samples were studied:

- Neat (W, T)
- W, T with 20% solvents by mass (WM, TM, WI, TI)
- 3 PMC mixes – Low content (4% by volume, PL), Medium content (13% by volume, PM) and High content (26% by volume, PH) for the four combinations WM, TM, WI, TI

1g and 2g of each of the above solutions was weighed out into polystyrene Petri dishes. For the size of dish used initial film depths were roughly ⅓ mm and ⅔ mm thickness. The dishes were covered over to limit evaporation. They were then left to cure for 4 weeks. After each week they were weighed to calculate the quantity of by-products that had evaporated from them during condensation/gelation. Notes and photographs were taken of the features and cracks that developed due to the shrinkages caused. The finer cracking features were also inspected using a standard laboratory microscope.

5.4.5 Measurement of relative viscosity

The relative viscosity of the treatments was measured using a timer and several glass pipettes. The pipettes' dimensions were determined to be standard as repeated measurement could not find significant differences between them. Marks were made at two points along the sides of each pipette, demarcating a volume of approximately 1.8±0.1ml. The time taken for this volume of each solution to pass through the 1mm diameter capillary at the bottom was measured. The viscosity was then assessed relative to the time taken for distilled water. All measurements were made at the same temperature, 293±1K. Chemical resistant gloves were used to protect the hands and small pieces of foam were used to insulate the burette. Each pipette was only used with one solution.

5.5 Preparation and application of consolidant treatments

The manufacturers' instructions are that the stone should be air dry before application. According to these instructions the consolidant should be applied until no additional material is absorbed after 1 minute. The excess should be wiped off with a solvent soaked sponge. If more is to be applied it should be done within 4 hours of application as a wet-in-wet process. The relative humidity should be greater than 40% and surfaces should be shaded from the sun so as to prevent rapid evaporation.

The consolidant treatments were applied using a natural bristle brush onto the most weathered face of each cube (whether parallel or perpendicular to the bedding plane), facing upright to avoid runoff problems. For some samples there was a strong bias towards one orientation, due to the anomalous nature of the weathering.

The natural bristle brush was regularly dipped in the solution and the surface was then brushed with it three times, left to absorb for a minute or two, then repeated for a total of three times and the surface wiped damp with a solvent-soaked sponge. Consolidant was further added until 'saturation' – when the absorption was so slow that the surface remained wet for 3 minutes without any noticeable decrease in the amount on the surface. Mass measurements were made to calculate the amount of consolidant absorbed. The samples were then covered over on all but the treated surfaces to control the evaporation of the reaction products. The treated surfaces were also loosely covered to protect against direct sunlight and possible draughts that may also cause excessive evaporation.

Solvents and nanoparticles were also added to the consolidant products and applied to the samples. The consolidant treatments chosen comprised the following contents shown in Table 5-6. The applied PMC solutions comprised approximately 26% (by volume) nanoparticles of silica and alumina in the ratio 4:1 by mass, using both TEOS products but only one solvent – MEK, as it had been a constituent in the products in the past, and as there were not enough samples to also test all of them with the Isopropanol. Isopropanol has higher viscosity, thereby defeating the purpose if used as a solvent. It is only relevant for use in PMC treatments.

Composition	% Product		% MEK		% Nanoparticles	
Treatment	Mass	Vol	Mass	Vol	Mass	Vol
Wacker	100.0	100.0	0.0	0.0	0.0	0.0
Wacker +MEK	80.0	83.2	20.0	16.7	0.0	0.0
Wacker PMC	86.8	67.1	10.5	6.7	2.5	26.2
Tego	100.0	100.0	0.0	0.0	0.0	0.0
Tego +MEK	80.0	84.0	20.0	16.0	0.0	0.0
Tego PMC	86.8	68.4	10.5	6.7	2.5	25.1

Table 5-6: Mass and volume percentage composition for applied consolidant treatments

The breakdown of the numbers of samples to which the consolidant products were applied is outlined in the following Table 5-7. The number of untreated samples is also included.

The evaporation of the treatment was hindered by covering the samples loosely with a sheet of aluminium foil to prevent both air circulation and heat transfer. The relative humidity of the laboratory was kept at approximately 40±5% RH for a few days until the hydrolysis process was practically completed. Occasional mass measurements were taken in order to determine the progress of gelation, as mentioned at the bottom of *Section 5.4.4*. The samples were left for 6 weeks before the treated properties were determined.

No. cubes: Sample	Treated with Wacker OH			Treated with Tegovakon V			Untreated	Total
	Neat	+MEK	PMC	Neat	+MEK	PMC		
Drumbane Grey	3	4	2	4	5	3	6	27
Drumbane Rusty (cubes)	2	2	1	2	1	2	2	12
Drumbane Rusty (prisms)	2	2	2	2	1	2	3	14
Manorhamilton	6	5	5	5	4	5	8	38
Clara Hill Grey	3	4	4	3	3	3	5	25
Clara Hill Yellow	2	2	2	2	2	2	4	16
Killaloe Buff	2	2	2	2	2	2	3	15
Killaloe Grey/Green	2	2	2	2	2	2	3	15
Killaloe Ochre	1	1	0	1	1	0	1	5
Killaloe Dark Grey	1	1	1	1	1	1	0	6
Total	24	25	21	24	22	22	35	173

Table 5-7: Numbers of cubes in each sample group treated by each of the consolidant products and treatments

The breakdown of the faces to which the consolidants were applied is presented in Table 5-8:

Treatment	Wacker		Wacker +MEK		Wacker PMC		Tego		Tego +MEK		Tego PMC		Total	
Sample	⊥	//	⊥	//	⊥	//	⊥	//	⊥	//	⊥	//	⊥	//
Drumbane Grey	0	3	1	4	0	2	4	1	0	5	1	1	6	16
Drumbane Rusty (Cubes)	0	2	1	1	0	2	2	1	0	1	1	1	4	8
Drumbane Rusty (Prisms)	2	0	2	0	2	0	2	0	1	0	2	0	11	0
Manorhamilton	3	2	3	2	3	2	4	2	2	3	4	2	19	13
Clara Hill Grey	0	3	0	4	0	4	0	3	0	3	0	2	0	19
Clara Hill Yellow	1	1	0	2	0	2	2	0	1	1	1	1	5	7
Killaloe Buff	0	2	0	2	0	2	1	1	2	0	0	2	3	9
Killaloe Grey-Green	2	0	0	2	1	1	1	1	2	0	2	0	8	4
Killaloe Ochre	1	0	0	1	0	0	1	0	1	0	0	0	3	1
Killaloe Dark Grey	1	0	1	0	1	0	0	1	1	0	0	1	4	2
Total	10	13	8	18	7	15	17	10	10	13	11	10	63	79

Table 5-8: Breakdown of orientation of faces to which consolidants were applied, generally the most weathered face for each cube – parallel (//) and perpendicular (⊥) to the natural bedding plane

The consolidants were predominantly applied to faces that were parallel to the natural bedding of the samples. Effectively this shows the orientation of the most weathered faces of cubes in proportion, as discussed in *Chapters 6* and *8*.

5.6 Methods to determine the success of consolidant treatment

5.6.1 Evaluation of physical properties of the treated samples

The density, porosity, capillary absorption and evaporation properties of the samples were again determined following treatment, using the methods in *Section 5.2.2.1.*

5.6.2 Water drop absorption test

Representative groups of samples were cut in two using a circular saw especially designed for cutting for geological analysis. The Water drop absorption test was employed to quantify any differences in absorption along the depth of the sample starting from the face of application. This was used to estimate the depth of penetration of the consolidants into the samples. (RILEM, 1980, Comm. 25-PEM, Test No. II.8a, Leroux *et al*, 2000, and Young *et al*, 2003)

The water drop absorption rate is defined as the absorption time of a known amount of water by the surface of a material and can be used to identify changes in the stone surface properties whether by treatment or weathering. The water absorption by capillarity is assumed to decrease slightly after pores are filled by consolidants, and vice versa when the pores are opened up by weathering. Times longer than 3 minutes may be affected by evaporation so if absorption has not occurred before then it may be reported as >3mins.

Rows of 0.01ml droplets of water were spread at depths of 5mm, 10mm, 20mm and 40mm from the application surface on the dried cube cross sections with a micropipette. The time taken for complete absorption of the droplets into the treated and untreated stone was measured. This was measured as the time from the placement of the droplet until all free water had been soaked into the cube, and the surface just appeared damp, not wetted. The depth of penetration was interpreted as being the distance (±1mm) from the surface of application where the average absorption time differed significantly compared to readings at greater depths.

5.6.3 Surface wetting test

Visual inspection of the surface wetting and drying effects in the cut cubes cross section were also carried out in order to estimate the depth of penetration, as per Leroux *et al* (2000) and Young *et al* (2003). This is based on the assessment of the intensity of reflected light from a porous surface. Where the pore walls are lined with consolidant the effective pore size is slightly reduced, thereby affecting the appearance of the surface when wet or drying. As a result after lightly splashing a cut surface with just enough water to wet it, some areas dry quicker than others. The distance from the treated surface to the boundary between the areas was noted (±1mm). This method was repeated several times to verify. If the profile was not the same across the cube a range for the values was noted.

According to this principle, the combined effects of both weathering and treatment can affect the appearance of stone cubes as the reflectance is altered by both material losses and changes in porosity. Some cubes were weathered to such an extent that the drying still occurred faster in the zone of penetration despite the presence of consolidant.

5.6.4 SEM and EDX analysis

Cross sections of the treated samples were analysed using a Scanning Electron Micoscope (SEM) with Electron Dispersive X-Ray (EDX) to observe the microstructure and compositional analysis of the cross section, noting in particular the lining of the pore walls with the consolidant and any variations in the samples. The model used was a Hitachi S-3500N variable pressure SEM. It has a resolution of 3.5nm at high pressure, and was equipped with a PGT SPIRIT X-ray microanalysis system EDX. The sandstone samples were not coated prior to analysis.

5.6.5 Evaluation of durability of the treated samples compared to the untreated samples

Salt crystallisation cycling was used in order to compare the durabilities of the treated and untreated samples, as per *Section 5.3* above. The treated faces were exposed above the level of the salt solution in order to concentrate weathering on the treated material. Any differences in weathering between treated and untreated samples were observed.

The density, porosity, capillary absorption and evaporation properties of the samples were again determined following weathering, using the methods in *Section 5.2.2.1*.

Chapter 6:

Results

6 *Results*

6.1 Characterisation of sandstone samples

6.1.1 Petrography

This section includes the petrographic composition and physical properties of the four sandstones studied.

6.1.1.1 Drumbane sandstone

The Drumbane sandstone is grey and rusty in colour with varying clay mineral, iron oxide and mica contents.

In the Grey type the quartz is fine to medium-grained well sorted, and is occasionally corroded. Interstitial clay minerals are distributed throughout. The cements are a combination of siliceous, argillaceous and ferruginous. There are low amounts of mica and no feldspars in this stone. There are also occasional fracture planes where there is poor quartz interconnection and scarce iron cements and clay (Table 6-1 and Figure 6-1).

Secondary alterations to this Grey type since deposition have resulted in a more open medium-fine pore structure: the Rusty type. The iron oxides are present as layers, lining large pores caused by the loss of fine quartz and clay minerals. It is this ferruginous content that gives the stone its pale rusty colour (Table 6-2 and Figure 6-2).

The pores are very fine in the clay matrix and medium-fine where clay matrix and quartz grains have been lost (Figure 6-2,2). The pores are generally angular and have low sphericity.

Drumbane Grey sandstone			
Constituent	Proportion	Size	Cement/Matrix
Quartz	60%	Medium – fine	<5% siliceous cements
Iron Oxide	6%	Medium – fine	Cementitious binder, secondary deposition
Mica	Occasional	-	Not visible in thin section
Clay matrix	30%	-	Interstitial, cohesive
Pores	4%	Fine – very fine	-

Table 6-1: Proportion and texture of constituent minerals and pores in Drumbane Grey sandstone

Drumbane Rusty sandstone			
Constituent	Proportion	Size	Cement/Matrix
Quartz	50+%	Medium - fine	<4% siliceous cements
Iron	15%	-	Cementitious binder, secondary deposition
Mica	Occasional	-	-
Clay matrix	15-25%	-	Interstitial, cohesive
Pores	10%	Medium - fine	-

Table 6-2: Proportion and texture of constituent minerals and pores in Drumbane Rusty sandstone

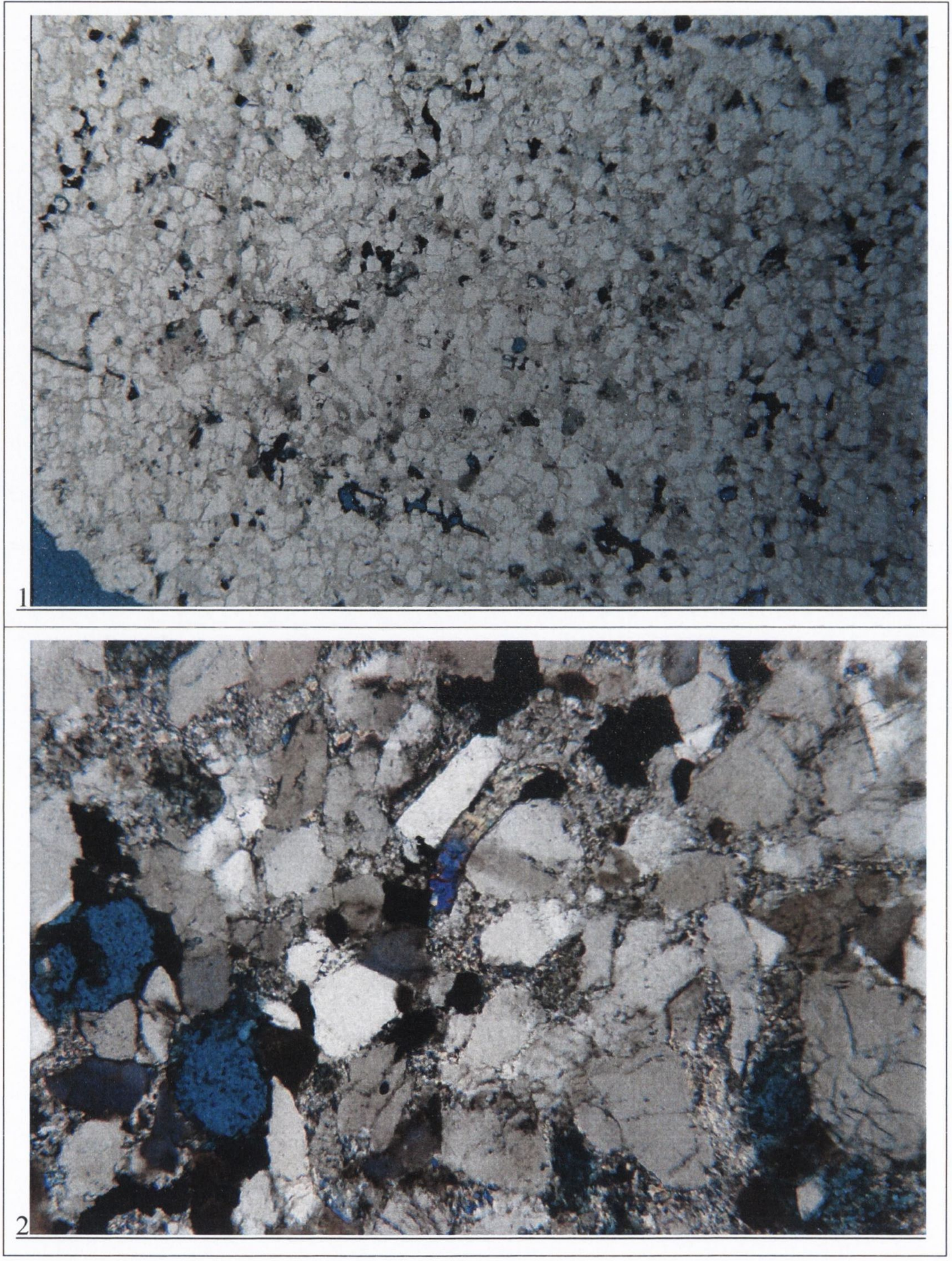


Figure 6-1: Photographs of Drumbane Grey sandstone thin section studied with petrographic microscope (1- 2x natural light, 2- 20x polarised light)

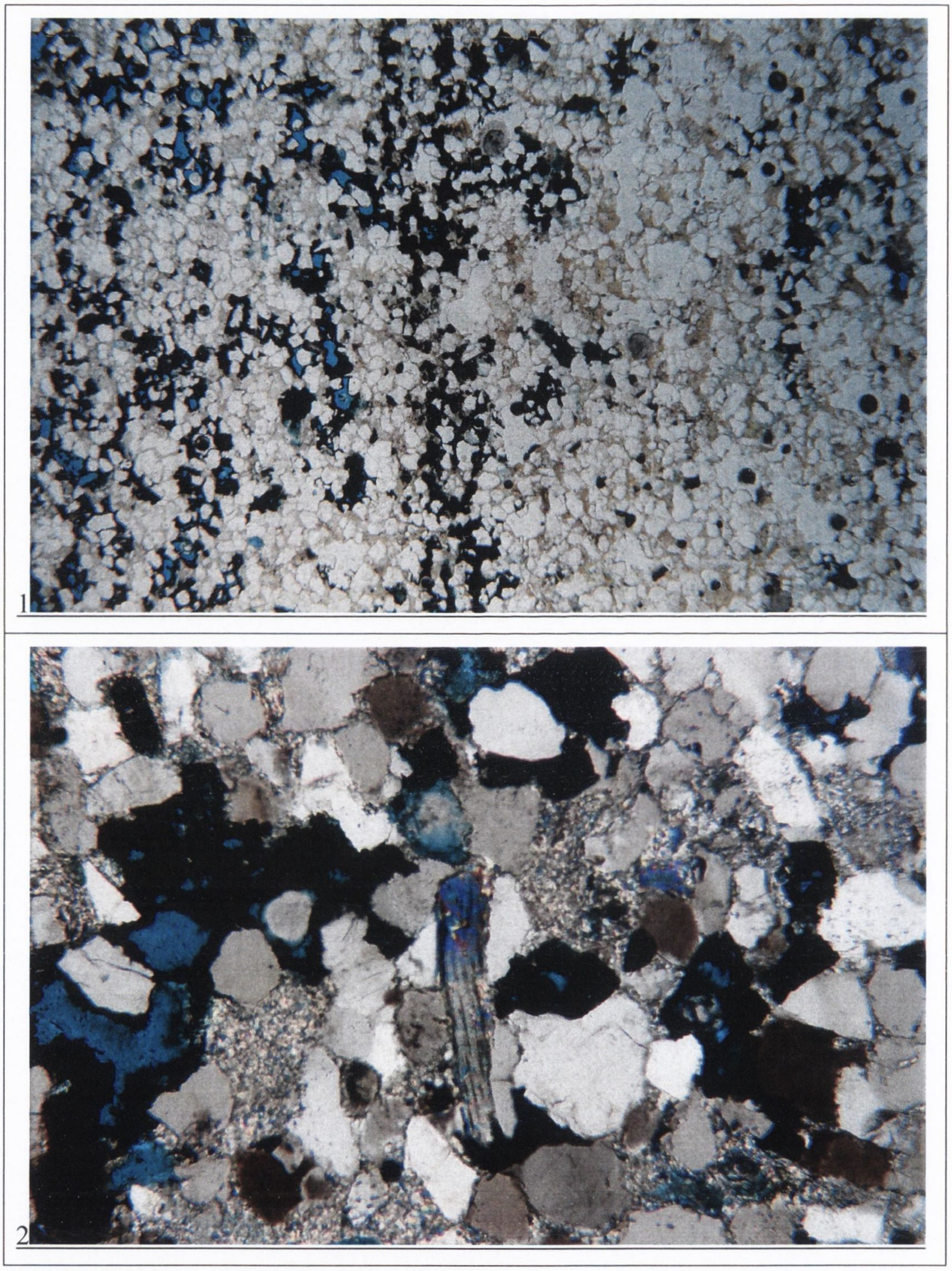


Figure 6-2: Photographs of Drumbane Rusty sandstone thin section studied with petrographic microscope (1- 2x natural light, 2- 20x polarised light)

6.1.1.2 Manorhamilton sandstone

The Manorhamilton sandstone is a fine- to medium-grained pale sandstone with sub-rounded to sub-angular grains of low sphericity, containing clay minerals, iron cements, and micas in a moderately sorted structure. This is shown in Table 6-3 and Figure 6-3 (1). The colour varies from grey to brown and sandy, depending mainly on the iron content. Variations can be seen as differences in colour along horizontal beds.

Figure 6-3 (2) shows the nature of the grains, cements and pores. The low clay matrix content results in a high primary porosity. The cements are siliceous and ferruginous, resulting in a strong but highly porous structure; the pores are medium to fine in size, sub-angular in shape and have a wide distribution throughout the stone. Larger pores are the result of poor or irregular packing.

The iron is present as fine spherical masses at interstices, as very fine coatings on quartz grains, and even as occasional large disordered masses.

Manorhamilton sandstone			
Constituent	Proportion	Size	Cement/Matrix
Quartz	70+%	Medium - Very fine	Sparsely cementing
Iron Oxide	<6%	Fine	Cementitious binder, secondary deposition
Mica	Occasional	-	-
Clay matrix	5-10%	-	Occasionally cohesive
Pores	12%	Fine - medium	-

Table 6-3: Proportion and texture of constituent minerals and pores in Manorhamilton sandstone

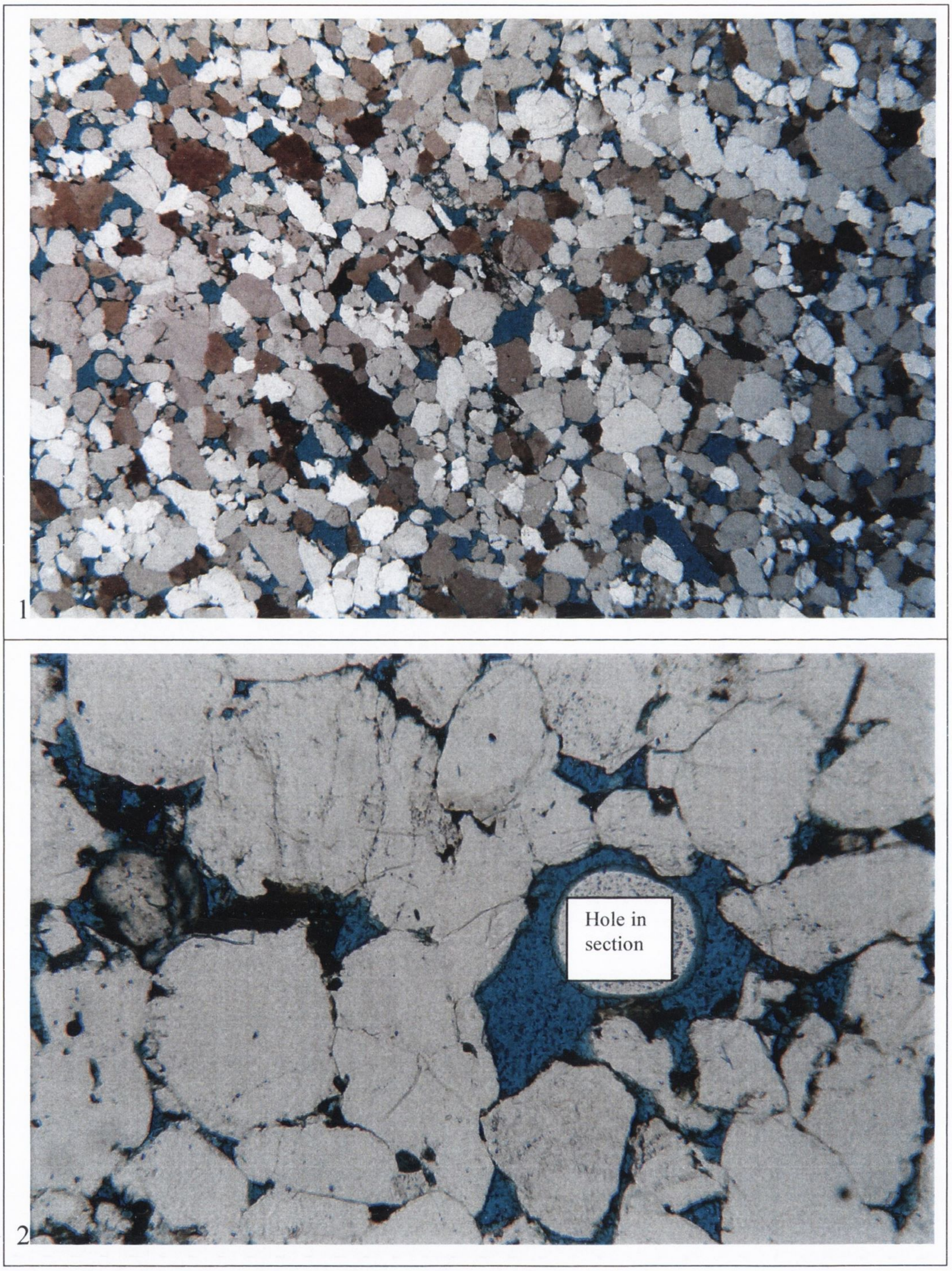


Figure 6-3: Photographs of Manorhamilton sandstone thin section studied with petrographic microscope (1- 2x polarised light, 2- 20x natural light, NB: hole in thin section in pore)

6.1.1.3 Clara Hill sandstone

The Clara Hill sandstone has a maximum quartz content of between 60% and 70%. Throughout the stone there is a noticeable difference in composition, according to the content of micas, iron oxides and clay matrix, as presented in Table 6-4.

Grey and white coloured samples can also include occasional rusty, yellow, or dark brown specks. The majority of particles are medium-fine in size, fairly well sorted and subrounded - subangular texture (Figure 6-4). The pores are fine to very fine. They have a wide size distribution but are occasionally poorly connected.

Clara Hill Grey sandstone			
Constituent	Proportion	Size	Cement/Matrix
Quartz	70-80%	Medium-fine	Trace cementitious binder (<1-2%)
Iron Oxide	7%	Fine	Cementitious binder
Mica	Occasional	-	-
Clay matrix	15%	-	Cohesive binder
Pores	5-7%	Fine	-

Table 6-4: Proportion and texture of constituent minerals and pores in Clara Hill Grey sandstone

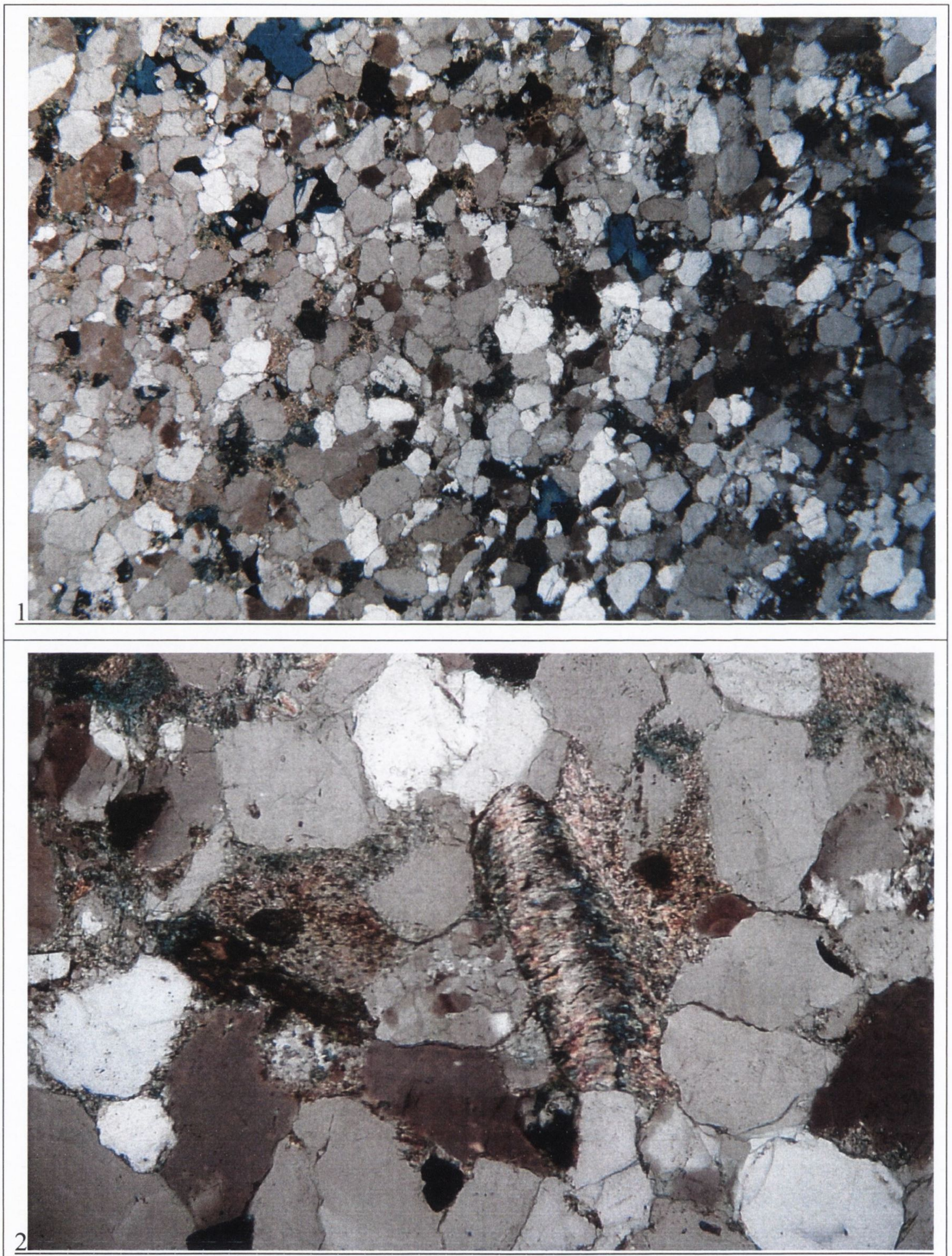


Figure 6.4: Photographs of Clara Hill Grey sandstone thin section studied with petrographic microscope (1- 2x polarised light, 2- 20x polarised light)

The Yellow variety contains medium sized particles that are well sorted. Their shape is sub-angular to angular and they have low sphericity. Rusty, white and grey specks were also visible throughout.

The pores are medium–large in size. They have a wide distribution due to the low amount of cementation between grains so the stone's density varies. The poorly cemented nature is evident in the high open porosity, as shown in Table 6-5 and Figure 6-5.

Clara Hill Yellow sandstone			
Constituent	Proportion	Size	Cement/Matrix
Quartz	60%	Medium	Occasional accessory silica cements (1-2%)
Iron Oxide	10-15%	Fine	Cementitious binder, secondary deposition
Mica	Occasional	-	-
Clay matrix	10%	-	Cohesive binder
Pores	10-15% to 25-30%	Coarse- fine	-

Table 6-5: Proportion and texture of constituent minerals and pores in Clara Hill Yellow sandstone

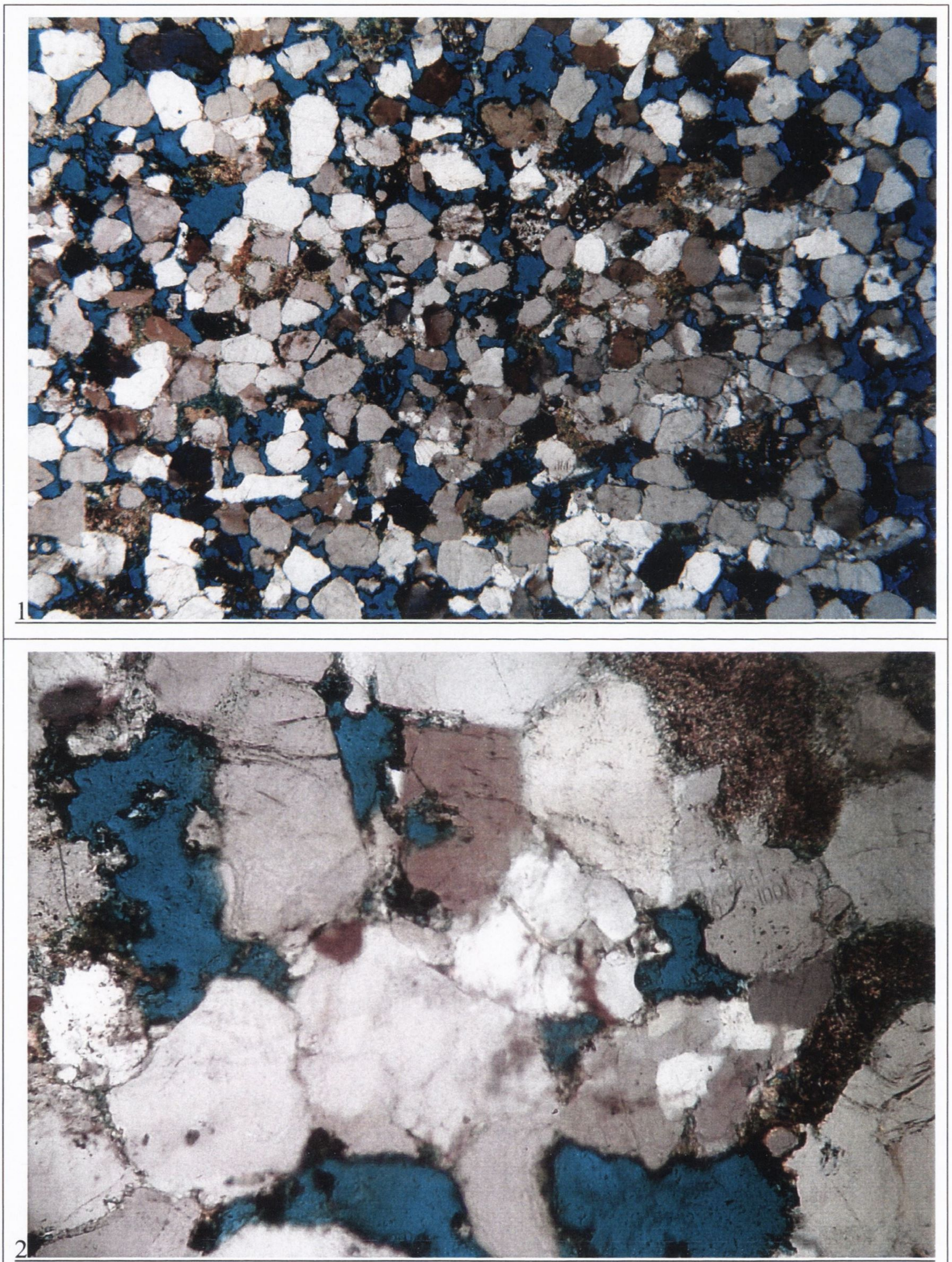


Figure 6.5: Photographs of Clara Hill Yellow sandstone thin section studied with petrographic microscope (1- 2x polarised light, 2- 20x polarised light)

6.1.1.4 Killaloe sandstone

The Killaloe sandstone has a quartz content of approximately 80% on average, with varying amounts of clay minerals, iron oxides and feldspars contributing to the large differences in colour. The majority of the stone is very compact with very fine-fine pores. This is primarily due to the dense packing of the quartz grains, many of which are intergrown.

The colours range from a pale buff with rusty brown striations (buff), to a deep ochreous red (ochre). There are also grey samples with green and black feldspar minerals (grey-green) and even darker ones with both compact and open material intrusions (dark grey).

The Buff sample is tightly packed and contains medium-fine quartz particles. There is a regular distribution of weathered clay matrix. Iron oxides are highly concentrated in parts and vary in form according to weathering. As a result the porosity is low and so strength is high (Figure 6-6). The proportions and textures of the constituents are presented in Table 6-6.

The Grey-Green samples have occasional irregular packing so they contain medium and more angular pores, although these have poor interconnectivity and some are sealed (Figure 6-7, 1). The dolomite and pore structure are also shown (2). The proportions and textures of the constituents are presented in Table 6-7.

The Ochre samples are also dense and low in porosity; however they do show evidence of secondary weathering in the occasional fissures and fracture planes. The fractures consist of exposed quartz grains lined with varying quantities of iron oxides.

The Dark Grey samples have medium-coarse pores in the open parts, but are medium to very fine in the dense parts. They are generally sub-rounded and of low to medium sphericity.

Killaloe Buff sandstone			
Constituent	Proportion	Size	Cement/Matrix
Quartz	80-85%	Medium – fine, negative skew	Cementitious, intergrown
Iron Oxide	5-10%	Fine	Cementitious
Clay matrix	Occasional	-	-
Mica	Occasional	-	-
Pores	1%	Fine – very fine	Contain iron and clays (refilled)

Table 6-6: Proportion and texture of constituent minerals and pores in Killaloe Buff sandstone

Killaloe Grey-Green			
Constituent	Proportion	Size	Cement/Matrix
Quartz	85%	Medium	Polycrystalline, cementitious binder
Iron Oxide	5-8%	Fine	Secondary deposition & weathering
Feldspars	5%	Medium	Microcline
Dolomite	Occasional	Fine	Cementitious, mixed with siliceous
Pores	2-5%	Fine - medium	-

Table 6-7: Proportion and texture of constituent minerals and pores in Killaloe Grey-Green sandstone

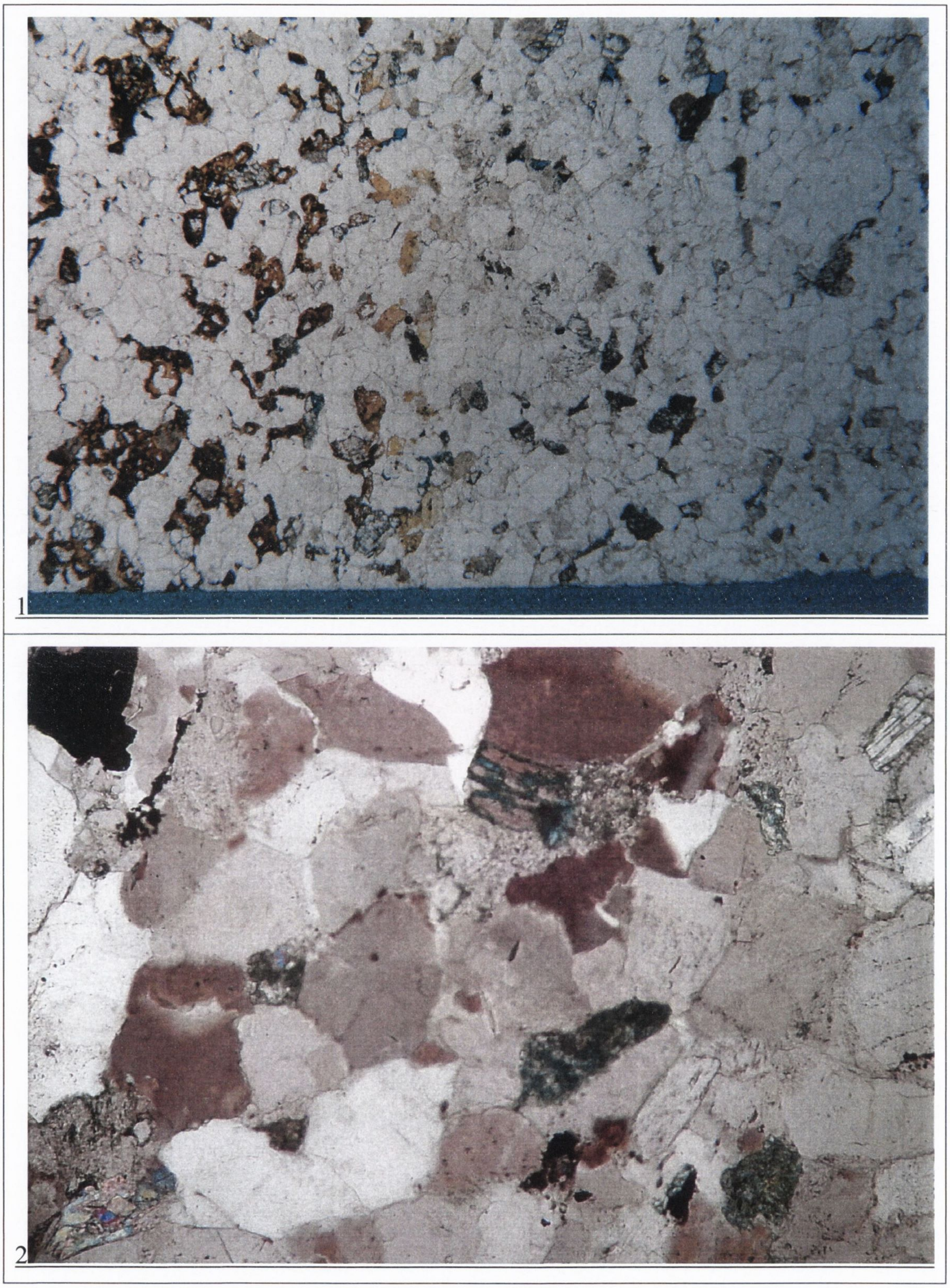


Figure 6.6: Photographs of Killaloe Buff sandstone thin section studied with petrographic microscope (1- 2x natural light, 2- 20x polarised light)

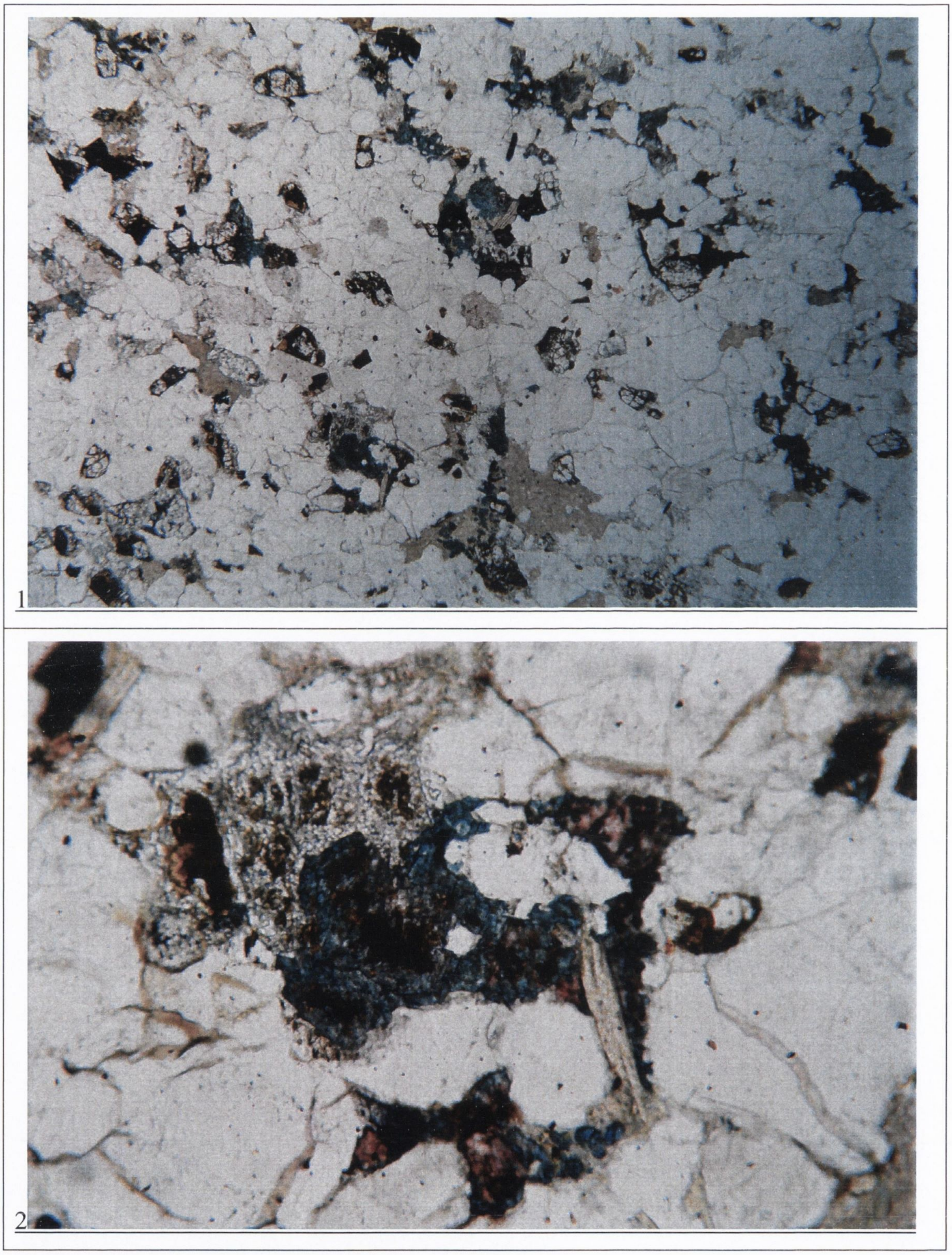


Figure 6.7: Photographs of Killaloe Grey-Green sandstone thin section studied with petrographic microscope (1- 2x natural light, 2- 20x natural light)

6.1.2 Mass structure properties

The mass properties of the sandstones are summarised in Table 6-8 below. The number of samples in each group is presented, showing the mean and range of values obtained for the mass, open porosity and apparent density of the cubes.

Sample	No. cubes	Cube mass (g)		Open porosity (%)		Apparent density (kg/m^3)	
		Mean	Min	Mean	Min	Mean	Min
			Max		Max		Max
Drumbane Grey	30	301.8	278.7	3.7	2.9	2561	2527
			316.7		4.4		2597
Drumbane Rusty (Cubes)	15	272.8	252.4	7.1	6.3	23~~21~~78	2336
			280.2		8.6		2405
Drumbane Rusty (Prisms)	14	368.5	333.8	8.9	8.2	2268	2254
			391.4		9.3		2284
Manorhamilton	45	293.0	250.8	11.0	9.9	2329	2309
			336.5		12.3		2349
Clara Hill Grey	27	328.7	280.1	4.7	4.0	2481	2456
			365.2		6.8		2508
Clara Hill Yellow	18	293.0	259.3	15.2	10.9	2188	2114
			326.6		17.7		2286
Killaloe Buff	23	373.5	340.4	2.3	1.9	2550	2527
			427.8		3.5		2571
Killaloe Grey-Green	17	368.0	351.2	1.5	1.3	2660	2607
			377.1		2.4		2693
Killaloe Ochre	5	334.9	326.4	2.7	1.8	2543	2528
			346.1		3.3		2551
Killaloe Dark Grey	6	363.2	338.7	8.3	1.9	2436	2317
			404.4		12.2		2633

Table 6-8: Mass structure properties of sandstone samples obtained

The ranges shown for the mass of the sample groups indicate the distribution in size for each sample group. The Drumbane Grey and Killaloe Grey-Green samples both had a narrow range, while the Manorhamilton and Killaloe Buff samples had the wide distributions in sample size, for example.

The Killaloe and Drumbane Grey samples have high apparent density, and conversely they have low porosity. The Clara Hill Yellow samples are the least dense. The variability in both open porosity and apparent density of the Drumbane and Clara Hill samples is evident when their varieties are compared. The dissimilarities in the Killaloe Dark Grey samples are reflected in the minimum and maximum values obtained for both porosity and density.

6.1.3 Moisture transfer properties

The moisture transfer properties of the samples are summarised in Table 6-9 on the next page. The capillary absorption coefficients and average rates of moisture transfer calculated over each of 2 consecutive 24 hour periods are presented.

The Manorhamilton and Clara Hill Yellow samples had the highest capillary absorption during the 1st 24 hours. The Killaloe Dark Grey sample also had occasionally high capillary absorption, but due to its variability it also had very low absorption rates. This may be of greater interest in relation to the role of moisture in weathering processes in the monuments, particularly at Clonfert.

The Drumbane Rusty and Killaloe Dark Grey samples had the highest evaporation rates during the 1st 24 hours. Evaporation during the 2nd 24 hours was highest in the Manorhamilton and Clara Hill Yellow samples. The Killaloe Grey-Green sample had the lowest evaporation rates.

Sample	No. cubes	Capillary absorption (g/m^2/s^{½})						Evaporation (g/m^2/hr)			
		Coefficient		1st 24 hours		2nd 24 hours		1st 24 hours		2nd 24 hours	
Drumbane Grey	30	8.0	2.6 11.4	4.6	3.8 5.8	1.6	0.5 2.9	35	22 51	11	6 17
Drumbane Rusty (Cubes)	15	9.6	4.9 18.5	6.7	5.6 8.4	3.8	3.1 4.5	67	48 96	31	27 42
Drumbane Rusty (Prisms)	14	14.8	8.9 19.5	7.5	6.3 8.4	3.0	1.5 4.4	58	44 67	30	22 38
Manorhamilton	45	12.7	7.7 21.4	9.1	6.2 12.0	0.6	0.1 4.0	37	28 65	34	21 48
Clara Hill Grey	27	7.1	4.8 7.7	5.9	4.7 8.8	3.2	1.1 4.2	23	17 31	12	8 23
Clara Hill Yellow	18	19.9	10.8 31.4	13.8	7.2 20.1	3.2	0.6 9.2	47	33 55	40	36 83
Killaloe Buff	23	3.5	2.4 5.4	2.6	2.1 3.2	1.3	0.8 1.6	22	19 34	7	5 13
Killaloe Grey/Green	17	2.9	1.7 4.0	1.8	1.4 2.3	0.8	0.2 1.3	13	10 20	2	1 8
Killaloe Ochre	5	5.6	3.1 8.7	2.5	2.2 2.8	0.6	0.3 0.7	38	23 45	6	4 9
Killaloe Dark Grey	6	23.7	4.0 45.2	5.8	2.1 7.8	2.3	0.7 7.9	65	18 131	40	14 68

Table 6-9: Moisture transfer properties of sandstone samples obtained (mean, minimum and maximum values)

6.1.4 Mechanical strength properties

The values determined for mechanical strength by crushing are summarised in Table 6-10 on the next page, using calculations [1] and [2] from *Section 5.2.2.2*. Insufficient numbers of cubes of the Killaloe Ochre and Dark Grey samples were available for crushing. The mode of failure of all samples was by shear, as conical parts remained after crushing.

Also shown is the surface hardness determined using the Schmidt hammer. The values obtained were in the upper end of the calibration chart. In this range the errors were approximately 10%. The surface hardness is between 1.1 and 1.2 times the compressive strength for all except the Manorhamilton sample. The Clara Hill Yellow samples they fractured due to the impact of the Schmidt hammer.

Sample	Loading							NDT
	No. cubes	Apparent density (kg/m^3)		Modulus (GPa)		Compressive strength (N/mm^2)		Surface hardness (N/mm^2)
Drumbane Grey	2	2564	2564	32	36	121	111	130±13
			2565		47		131	
Drumbane Rusty	2	2367	2366	26	16	70	68	76±8
			2367		36		72	
Manorhamilton	9	2331	2325	36	26	105	91	90±9
			2349		45		122	
Clara Hill Grey	3	2463	2456	15	10	62	49	80±8
			2476		18		76	
Clara Hill Yellow	2	2208	2195	13	10	50	48	-
			2221		15		52	
Killaloe Buff	7	2553	2534	47	23	156	140	170±17
			2569		63		221	
Killaloe Grey-Green	2	2654	2642	32	23	108	89	130±13
			2666		41		125	
Killaloe Ochre	0	-	-	-	-	-	-	130±13
			-		-		-	
Killaloe Dark Grey	0	-	-	-	-	-	-	120±12
			-		-		-	

Table 6-10: Compressive strength and modulus of elasticity of sandstone samples, showing the number of cubes of each and their apparent densities, and comparing them with measurements of surface hardness taken by the hammer rebound test where available

The Clara Hill Grey and Drumbane Rusty samples had lower values for the mechanical strength properties, while the Killaloe and Drumbane Grey samples had higher values. The variation in the values for modulus of elasticity in the Drumbane and Killaloe varieties may be cause for concern in the monuments where they are side-by-side. Such variability can increase the vulnerability of the stone to weathering, depending on the stresses to which they are subjected.

6.2 Artificial weathering of sandstone samples

6.2.1 Salt crystallisation cycling

The samples were subjected to the salt crystallisation cycles, as described in *Section 5.3*. The net result can be seen in the following graph plotting the percentage change in the average mass of the samples during the accelerated weathering cycles (Figure 6-8).

Steady increases in salt content and hence sample mass were observed in the majority of samples until the 6-8th cycles. Sample mass then levelled off until the 8-11th cycles, and material losses occurred during the final 3-5 cycles.

Some samples lost material after as few as 4-5 cycles, as in the case of the Clara Hill Yellow samples – these were omitted from the immersion cycles after the 9th one in order to protect the cubes from total disintegration.

The balance in mass between salt gains and material losses in the Clara Hill Grey and Killaloe samples remained positive during the cycles.

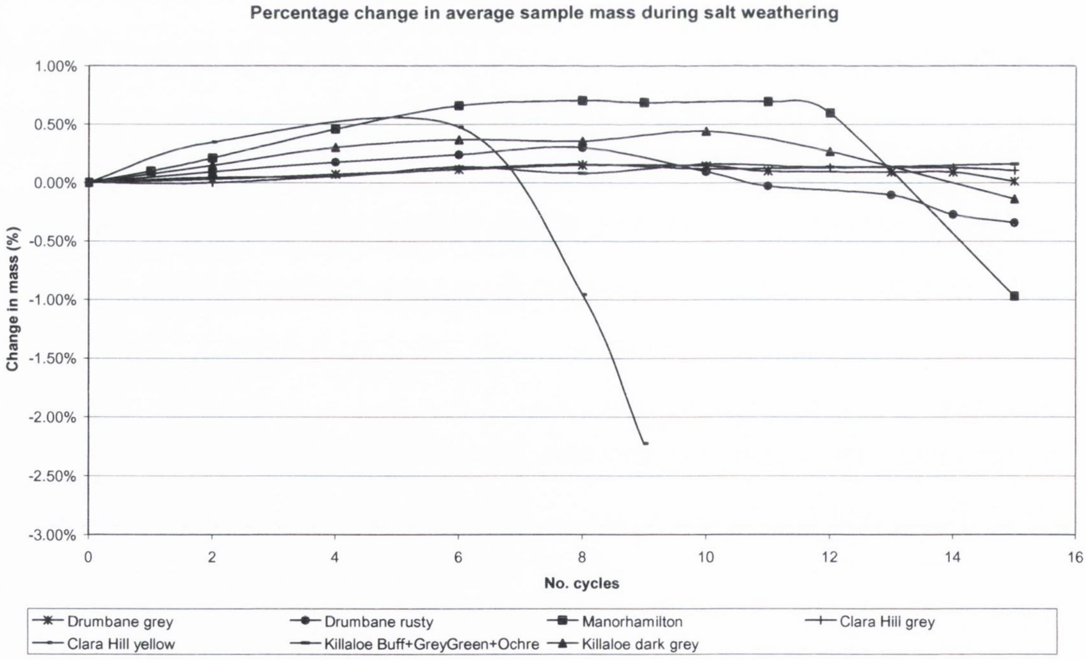


Figure 6.8: Percentage change in average sample mass during salt crystallisation cycles

6.2.2 Washing of salts from samples

Following completion of the salt crystallisation cycling the samples were washed by a combination of both long term immersion in constantly flowing water and washing of efflorescent salts after drying at room temperature (as recommended in RILEM PEM-25 and BS EN 12370:1999). In order to assure greater removal of the salts further washing was carried out than specified in either standard.

The further washing of the samples caused further damage; however, it was necessary to free the samples from salts to be able to assess the weathered properties accurately and also so that the application of consolidant products would not be compromised.

Conductivity measurements were taken at various stages during washing in order to monitor the rate of removal of salts from the samples, as plotted in Figure 6-9. A conductivity of 50 μS/cm is equivalent to a salt content of 0.14 g/kg (or 0.00014 %).

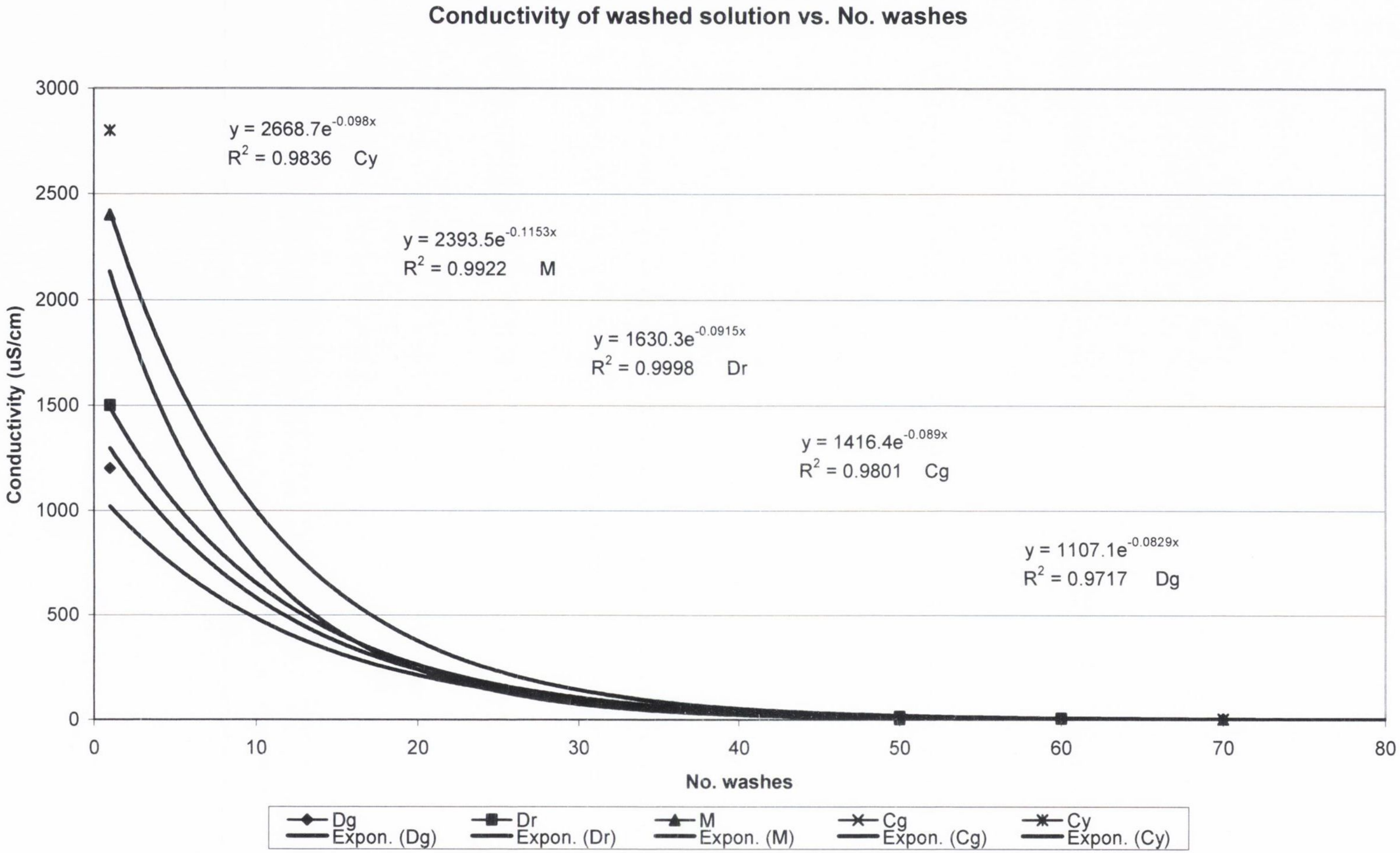


Figure 6.9: Exponential fit curves of conductivity measurements taken during washing of samples

The variety of decay types observed in the samples following artificial weathering suggested that there was a great difference in the durability of the sandstones. These are discussed further in *Chapter 8: Discussion – Durability and weathering of Irish sandstones whether treated or untreated.* A higher frequency of fracturing was noted in certain samples – see Table 6-11:

Sample	Principal decay type	Secondary decay types
Drumbane Grey	Fracturing	Flaking
Drumbane Rusty	Differential erosion	Fracturing Granular disintegration
Manorhamilton	Flaking	Differential erosion Mineral discolouration
Clara Hill Grey	Fracturing	Flaking Granular disintegration Mineral discolouration
Clara Hill Yellow	Differential erosion	Granular disintegration
Killaloe Buff	Mineral discolouration	-
Killaloe Grey-Green	Differential erosion	Mineral discolouration
Killaloe Ochre	Flaking	Differential erosion
Killaloe Dark Grey	Differential erosion	Granular disintegration

Table 6-11: Principal and secondary decay types observed in samples due to weathering

6.2.3 Properties of weathered sandstone samples

The sandstone properties changed significantly as a result of weathering. The Killaloe samples were the most durable and showed the least changes in the properties measured, while the Clara Hill Yellow samples were least durable showing the greatest changes.

6.2.3.1 Changes in mass structure due to weathering

Almost all samples experienced loss of material due to weathering, primarily from the outer surfaces. The changes in cube mass, porosity and density are presented in Table 6-12 on the next page.

Comparing the mean cube masses of the unweathered (U) and weathered (W) samples it is observed that the Killaloe Buff samples suffered least amount of material loss because of the artificial weathering. Higher losses occurred in the Drumbane Rusty (Prisms), Manorhamilton and Clara Hill Yellow samples.

The increases in open porosity seem to correspond well with the decreases in apparent density in all of the Drumbane, Manorhamilton and Clara Hill samples. It is assumed that of these, the changes in the Manorhamilton samples were lesser because of greater interconnectivity in the pores and higher uniformity of mass structure. The changes were greater in the Drumbane Rusty (Prisms) samples. This may be due to dimensional effects, making this sample less comparable with the others.

On inspection it was noticed that in the Killaloe samples the open porosity was decreased following weathering, while their apparent density was increased. Considering that they suffered very low material losses, it appeared that the Killaloe samples retained an appreciable quantity of salts deep in their interior that the washing failed to remove. It is reasonable that the salts be more difficult to remove from the Killaloe sandstones because of the reliance on ionic conductivity to transport the salts from within the samples.

This combination of factors highlights the fact that Killaloe samples are both too dense and too strong in their current condition to require consolidation treatment. Throughout the rest of this thesis Killaloe data will only be presented where relevant.

It is possible that the porosities of the other samples were also underestimated due to the presence of salts. Such inconsistencies are not so obvious however.

Sample	No. cubes	Cube mass (g)				Open porosity (%)				Apparent density (kg/m^3)			
	U∩W	Unweathered		Weathered		Unweathered		Weathered		Unweathered		Weathered	
Drumbane Grey	26	301.8	278.7 316.7	299.5 *-0.7%*	277.8 314.7	3.7	2.9 4.4	4.1 *+11%*	3.1 5.1	2561	2527 2597	2556 *-0.2%*	2509 2588
Drumbane Rusty (Cubes)	12	272.4	252.4 280.2	266.3 *-2.2%*	244.6 274.8	8.0	6.3 8.6	8.6 *+8%*	7.6 9.9	2378	2336 2405	2355 *-0.1%*	2322 2430
Drumbane Rusty (Prisms)	14	368.5	333.8 391.4	346.1 *-6.0%*	310.4 378.4	8.9	8.2 9.3	13.0 *+46%*	11.6 14.5	2268	2254 2284	2240 *-1.1%*	2206 2263
Manorhamilton	38	293.0	250.8 336.5	282.7 *-3.5%*	244.1 323.8	11.0	9.9 12.3	11.6 *+39%*	9.1 13.2	2329	2309 2347	2314 *-0.6%*	2275 2346
Clara Hill Grey	22	324.4	289.9 365.2	319.6 *-1.5%*	284.6 360.4	4.6	4.0 5.6	6.4 *+8%*	3.2 9.7	2485	2456 2508	2441 *-1.6%*	2404 2488
Clara Hill Yellow	16	293.0	259.3 326.6	268.2 *-8.5%*	219.6 327.6	15.2	10.9 17.7	16.4 *-9%*	9.2 19.5	2188	2114 2286	2168 *-0.9%*	2081 2320
Killaloe Buff	13	373.5	340.4 427.8	373.1 *-0.1%*	340.0 427.4	2.3	1.9 3.5	2.1 *-7%*	1.8 2.3	2550	2527 2571	2551 *0%*	2531 2568
Killaloe Grey/Green	14	368.0	351.2 377.1	366.8 *-0.3%*	350.0 375.7	1.5	1.3 2.4	1.4 *-30%*	1.2 1.7	2660	2607 2693	2661 *0%*	2632 2701
Killaloe Ochre	5	334.9	326.4 346.1	333.9 *-0.3%*	325.1 344.9	2.7	1.8 3.3	1.9 *-22%*	1.7 2.2	2543	2528 2551	2545 *+0.1%*	2528 2554
Killaloe Dark Grey	6	363.2	338.7 404.4	357.2 *-1.7%*	327.6 403.8	8.3	1.9 12.2	6.5 *-16%*	1.5 9.6	2436	2317 2633	2442 *+0.2%*	2318 2634

Table 6-12: Comparison of mass structure properties of unweathered (U) and weathered (W) sandstone samples (mean, minimum and maximum values)

6.2.3.2 Extent of weathering observed in samples

The decay from the samples resulted in the loss of material to varying degrees in the samples. The losses caused by the artificial weathering are shown in Table 6-13 on the next page. The losses are shown as a percentage of the unweathered sample masses, and also per unit surface area. The mass loss per unit area is shown for both the exposed top surface of the cubes above the level of immersion, and for the surface area over which appreciable material losses were observed. An estimate of the affected areas was calculated using photographic records and the dimensions acquired during measurements of the moisture transport properties.

Despite focussing the artificial weathering on one surface by using partial immersion, in many cases mass losses were not limited to the exposed surface. Most samples were also heavily affected in the top 2-5mm on the four sides along and below the level of the salt solution.

Furthermore, in most samples, at least a minor amount of material was lost on all other surfaces. The majority of these losses on other surfaces were simply observed as being a slight increase in the exposed pores sizes. The most susceptible areas were those near the edges of the cubes where evaporation is easier due to greater exposure of the pores, resulting in rounded edges.

Sample	No.	Cube mass (g)				Exposed surface (*10^{-5} m^2)		Mass loss/ exposed area (g/m^2)		Extent of weathered surfaces (*10^{-5} m^2)		Mass loss/ weathered area (g/m^2)	
	U∩W	Unweathered		Weathered									
Drumbane Grey	26	301.8	278.7	299.5	277.8	237	225	957	373	991	561	215	73
			316.7	*-0.7%*	314.7		245		1991		1433		586
Drumbane Rusty (Cubes)	12	324.8	252.4	266.3	244.6	237	222	2590	1476	1163	1043	504	311
			280.2	*-2.2%*	274.8		241		4138		1310		763
Drumbane Rusty (Prisms)	14	368.5	333.8	346.1	321.8	324	312	6241	3287	1533	1487	1316	705
			391.4	*-6.0%*	378.4		337		11070		1597		2330
Manorhamilton	38	293.0	250.8	282.7	244.1	247	228	3902	888	1279	975	779	156
			336.5	*-3.5%*	323.8		278		13148		1529		3086
Clara Hill Grey	22	326.0	280.1	319.6	270.9	261	240	3389	634	1270	860	643	108
			381.7	*-1.5%*	377.9		291		28069		1602		4226
Clara Hill Yellow	16	293.0	259.3	268.2	219.6	264	243	10812	1099	1437	1316	1973	196
			326.6	*-8.5%*	327.6		278		28338		1502		5039
Killaloe Buff	13	373.5	340.4	373.1	340.0	282	263	143	0	1244	745	35	0
			427.8	*-0.1%*	427.4		295		197		1596		60
Killaloe Grey/Green	14	368.0	351.2	366.8	350.0	268	261	423	100	1453	1061	77	26
			377.1	*-0.3%*	375.7		275		1201		1621		225
Killaloe Ochre	5	334.9	326.4	333.9	325.1	257	254	415	315	1533	1500	70	51
			346.1	*-0.3%*	344.9		267		512		1566		85
Killaloe Dark Grey	6	363.2	338.7	357.2	327.6	280	273	2173	221	1485	1211	396	50
			404.4	*-1.7%*	403.8		286		4053		1659		669

Table 6-13: Comparison of changes in cube mass and the corresponding change in mass per unit surface area due to weathering of sandstone samples over the exposed surfaces, and the full extent of the weathered surfaces (Mean, minimum and maximum values)

6.2.3.3 Changes in moisture transfer properties due to weathering

The capillary absorption rates of the weathered samples are compared to those of the unweathered samples in Table 6-14 on the next page. A similar comparison is presented for evaporation rates on the following pages.

6.2.3.3.1 Capillary absorption

The capillary absorption of the Drumbane sandstone was greatly increased due to fracturing. Fractures running perpendicular to the bedding enabled even greater absorption in the Rusty samples.

Weathering decreased absorption in the Manorhamilton sandstone during the 1st 24 hours, but increased later absorption such that the same amount of moisture was absorbed during the 48 hour period.

The Clara Hill samples had such high rates of absorption in the short term that the absorption during the 2nd 24 hours was lower, compared to the unweathered values. This was due to a combination of fracturing and rougher surfaces. In the Yellow sample, long term absorption was reduced because excessive losses created rougher outer surfaces. Hence the depth and volume of sandstone through which absorption could occur was reduced.

The Killaloe Buff sample absorbed more moisture in the long term, as did the Killaloe Ochre sample. The amount of moisture absorbed over 48 hours in the Killaloe Grey-Green and Killaloe Dark Grey samples was reduced, despite having higher rates prevailing during the first few hours.

Changes to the capillary absorption of the samples seemed to be contrasting when examined over the 1st or 2nd 24 hours. It is assumed that for this reason most of the data for later absorption rates is redundant.

Such changes were not observed in some of the Killaloe samples, so it is estimated that the reductions in absorption were also caused by the presence of salts.

Sample	No. cubes	Coefficient ($\mathrm{g/m^2/s^{1/2}}$)				1st 24 hours ($\mathrm{g/m^2/s^{1/2}}$)				2nd 24 hours ($\mathrm{g/m^2/s^{1/2}}$)			
	U∩W	Unweathered		Weathered		Unweathered		Weathered		Unweathered		Weathered	
Drumbane Grey	26	8.0	2.6 11.4	11.5 *+44%*	4.4 15.8	4.6	3.8 5.8	5.0 *+9%*	3.3 7.8	1.6	0.5 2.9	1.3 *-19%*	0.1 2.6
Drumbane Rusty (Cubes)	12	9.6	4.9 18.5	42.2 +340%	8.9 57.7	6.7	5.6 8.4	9.5 *+42%*	6.2 11.5	3.8	3.1 4.5	2.4 *-37%*	0.3 4.6
Drumbane Rusty (Prisms)	14	19.5	8.9 20.9	50.9 *+161%*	22.8 77.7	7.5	6.3 8.4	13.3 *+77%*	10.6 17.4	3.0	1.5 4.4	1.0 *-67%*	0.4 3.6
Manorhamilton	38	12.7	7.7 21.4	9.5 *-25%*	6.8 66.9	9.1	6.2 12.0	9.0 *-1%*	2.8 12.6	0.6	0.1 4.0	2.5 *+317%*	0.4 12.6
Clara Hill Grey	22	7.1	4.8 7.7	31.1 *+338%*	7.6 63.5	5.9	4.7 8.8	7.8 *+32%*	6.2 8.7	3.2	1.1 4.2	3.0 *-6%*	0.3 9.0
Clara Hill Yellow	16	19.9	10.8 31.4	38.1 *+91%*	25.8 57.5	13.8	7.2 20.1	11.6 *-16%*	7.5 16.2	3.2	0.6 9.2	2.6 *-19%*	0.9 5.9
Killaloe Buff	13	3.5	2.4 5.4	2.1 *-40%*	1.0 4.1	2.6	2.1 3.2	2.7 *+4%*	2.1 3.3	1.3	0.8 1.6	1.7 *+31%*	0.6 2.1
Killaloe Grey-Green	14	2.9	1.7 4.0	3.0 *+3%*	1.9 6.5	1.8	1.4 2.3	1.6 *-114%*	1.3 2.3	0.8	0.2 1.3	0.4 *-50%*	0.2 0.6
Killaloe Ochre	5	5.6	3.1 8.7	3.7 *-34%*	1.9 7.2	2.5	2.2 2.8	2.4 *-4%*	2.1 2.7	0.6	0.3 0.7	0.9 *+50%*	0.5 1.3
Killaloe Dark Grey	6	23.7	4.0 45.2	16.2 *-32%*	5.7 22.7	5.8	2.1 7.8	4.9 *-16%*	1.4 6.9	2.3	0.7 7.9	1.7 *-26%*	0.1 7.1

Table 6-14: Comparison of capillary absorption of unweathered (U) and weathered (W) sandstone samples (mean, minimum and maximum values)

6.2.3.3.2 Evaporation

As shown in Table 6-15 on the next page, the evaporation was slightly higher in all of the Drumbane samples. The surface dimensions of the Rusty Cubes and Rusty Prisms were responsible for differences in the rates during the 2^{nd} 24 hours: moisture was held in the inner fractures of the cubes, while the rates remained constant in the Prisms due to their greater surface/volume ratio.

Evaporation was over 60% higher in the weathered Manorhamilton sandstone.

The high surface area in the Clara Hill samples caused evaporation to increase significantly compared to the unweathered values.

Evaporation from the Killaloe samples was changed to various extents; rates were increased in the Buff samples, reduced in the Dark Grey ones, and delayed in both the Grey-Green and Ochre ones.

Sample	No. cubes	1^{st} 24 hours ($g/m^2/s^{½}$)				2^{nd} 24 hours ($g/m^2/s^{½}$)			
	U∩W	U		W		U		W	
Drumbane Grey	26	35	22 51	40 *+14%*	26 58	11	6 17	12 *+9%*	8 21
Drumbane Rusty (Cubes)	12	67	48 96	87 *+30%*	73 101	31	27 42	23 *-26%*	19 29
Drumbane Rusty (Prisms)	14	58	44 67	68 *+17%*	59 78	30	22 38	70 *+133%*	58 80
Manorhamilton	38	37	28 65	60 *+62%*	49 82	34	21 48	57 *+68%*	20 79
Clara Hill Grey	22	23	17 31	56 *+143%*	18 75	12	8 23	23 *+92%*	161 53
Clara Hill Yellow	16	40	33 55	66 *+65%*	41 93	58	36 83	50 *-14%*	12 89
Killaloe Buff	13	22	19 34	25 *+14%*	22 29	7	5 13	8 *+14%*	6 11
Killaloe Grey/Green	14	13	10 20	13 *0%*	10 17	2	1 8	4 *+100%*	3 8
Killaloe Ochre	5	38	23 45	24 *-37%*	21 27	6	4 9	7 *+17%*	6 7
Killaloe Dark Grey	6	65	18 131	65 *0%*	15 102	40	14 68	24 *+40%*	5 45

Table 6-15: Comparison of evaporation rates of unweathered (U) and weathered (W) sandstone samples (mean, minimum and maximum values)

6.3 Consolidation of sandstone samples

The data from the consolidant treatment of the samples presented here starts with the characteristics of the treatments chosen and the details of the application. The curing of the treatments was monitored and the changes in the sandstone properties as a result of consolidation were measured. The depth of penetration of the consolidant was assessed in cross-sections, as explained in *Sections 5.6.2* and *5.6.3*. Finally, in order to determine the durability of the consolidated samples, these were subjected to further weathering by salt crystallisation, as per the method in *Section 5.3*.

6.3.1 Characteristics of consolidant gels

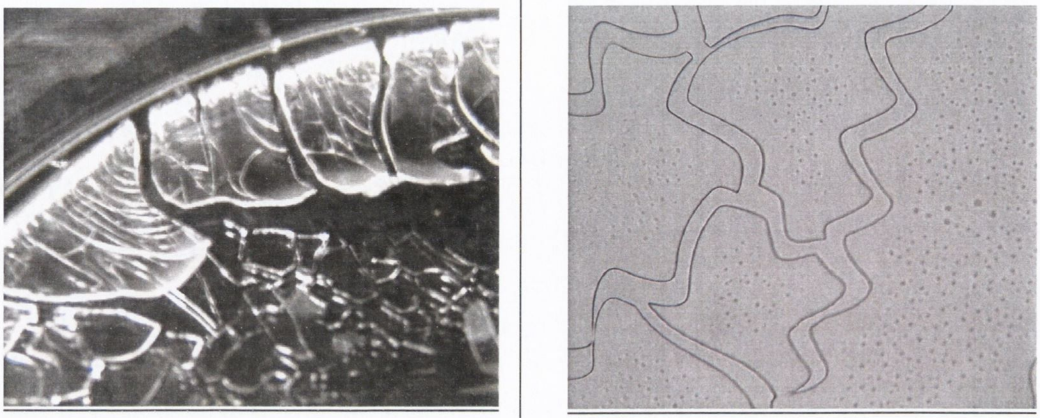
The cracking of the gel plates due to TEOS condensation provided qualitative information on the behaviour of the products, solvents and PMC nanoparticle contents.

6.3.1.1 TEOS gel plates

The gels containing just TEOS were fully transparent. The Tegovakon gels condensed and gelled slower, staving off cracking much longer than the Wacker gels. The evaporation from the surface of the Wacker gel was clearly more uniform, indicating that the condensation reactions were also progressing uniformly throughout the gel.

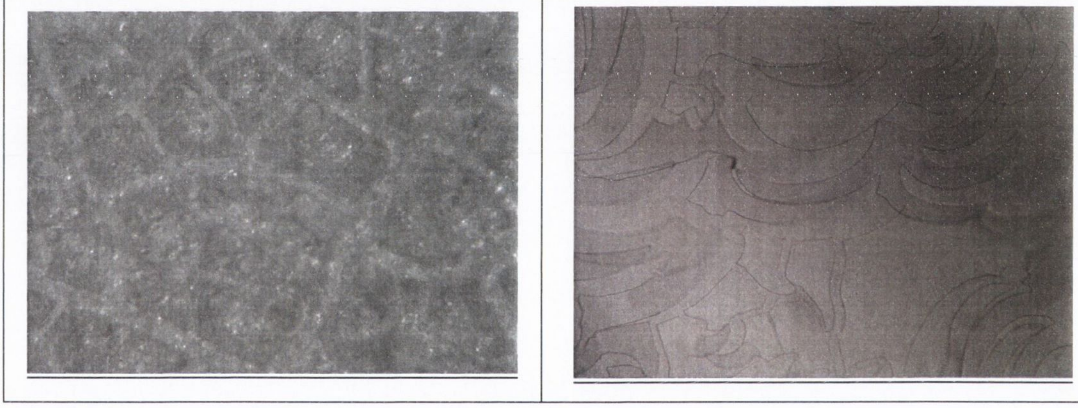
Where thinner, the Wacker gel cracked into tiny little pieces, curling and cracking because of the condensation and evaporation processes. Thicker parts remained more solid, with little or no breaking and 'curling'. With time individual pieces did shrink and curl slightly. Minute blemishes developed on the surface of the Wacker gel (Figure 6-10, 1).

Where thinner, the Tegovakon gel formed small random 'wave'-like cracking patterns (Figure 6-10, 2). This gel was thicker around the edges due to Tegovakon's liquid properties and this subsequently influenced cracking. When the thicker Tegovakon gel eventually did crack it was warped and had split across the midsection into a few large pieces. It eventually developed frequent, very fine, radial cracks near the edge. A covering of fine droplets was also observed on the Tegovakon gels (Figure 6-10, 2).



1 Wacker

2 Tegovakon



3 Wacker+MEK

4 Wacker+Isopropanol

Figure 6.10: Images of cracking patterns in gel plates 4 weeks after preparation (1- close-up isometric view, 2-4- viewed at 20x magnification under compound microscope)

6.3.1.2 TEOS +solvent gel plates

The gels containing Wacker+MEK were observed to develop a hazy white opaque film next to the dish, irrespective of the presence of nanoparticles. These gels quickly developed widespread 'micro-cracking', with a crystalline appearance that looked like the layout of a town on a map viewed from afar (Figure 6-10, 3). This occurrence may have been due to interactions between the products and the Petri dish.

The surfaces of the gels prepared with Isopropanol appeared smoother than the gels containing MEK, regardless of other contents. Random cracking patterns like 'bananas' appeared in the Wacker+Isopropanol gels however, with interlinking planar pieces fitted loosely like a crumbling jigsaw. This would suggest that variable shear stresses were induced during condensation and evaporation (Figure 6-10, 4).

6.3.1.3 PMC gel plates

Differences were observed according to the TEOS products in the PMC gel plates: the Wacker gels curled up due to surface tension effects from evaporation, forming typical u-shaped arcs. On the other hand the Tegovakon gels often developed n-shaped profiles, held by the reinforced rim of the outer edge (due to greater surface tension with the dish) and arcing towards the centre in pie-shaped wedges (Figure 6-11, 1).

Nonetheless the presence of nanoparticles enabled the gels to warp slightly while still compliant so the effects of 'curling' and 'rolling' were greater in the PMC gels. The ability of the PMC gels to deform and sustain greater strains highlights the significant gain in modulus afforded to the gel by the particles.

Low content gels were primarily transparent but small clusters of the aggregated nanoparticles were visibly distributed throughout. Cracking was occasionally observed near concentrations of agglomerated particles, as shown in Figure 6-11 (2). It is possible, although certainly not proven, that the agglomerations increase the ability of the gel to deform locally, but adjacent parts of the gel where particle content is much lower cannot withstand such strains and thus crack. This possibly demonstrates a 'double-edged sword' phenomenon: the increase in strain induced locally by the particle content may cause cracking to occur, even though the particles have served their purpose in reducing cracking where present. Perhaps the key factor in PMC application is particle dispersion as highlighted by Ke & Stroeve (2005).

Medium content gels were less transparent. The solvent type had a strong influence on this: the gels containing MEK were mostly opaque with irregular distribution of the particle agglomerations, while the gels containing Isopropanol were more transparent because the agglomerations were smaller and better distributed throughout the gel. Some of the finer pieces were rolled up tight (Figure 6-11, 3).

High content gels were even less transparent and in places appeared opaque due to the presence of highly agglomerated particles. The sizes of the agglomerations were widely distributed in the gels containing Isopropanol. Rolling and curling were also present. In some parts, the gels managed to wrap around themselves as much as 2-3 times (Figure 6-11, 4).

The radial shrinkage of the samples was monitored for as long as possible: i.e. while the gel plates were sufficiently unbroken. After 1 week the Wacker samples had shrunk by 5-10%, and at 3 weeks it was 30-35%. For the Tegovakon samples these values were 6-10% and 17-23% respectively.

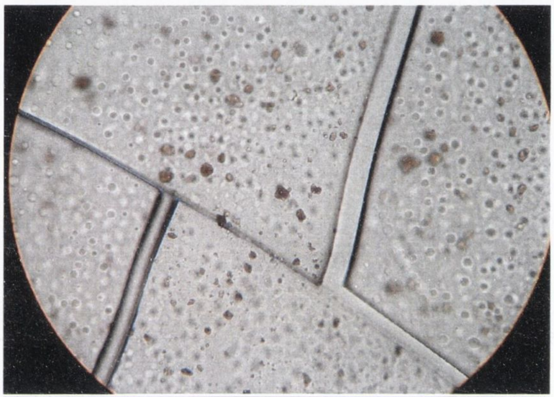
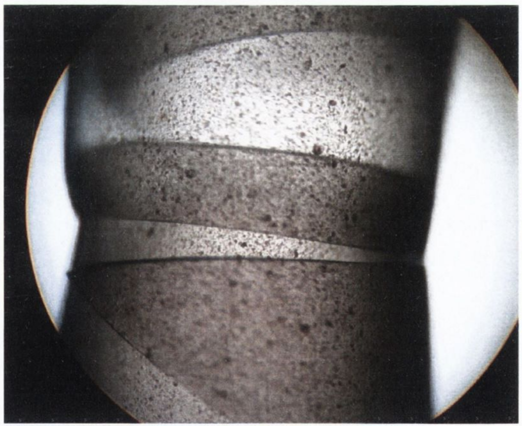
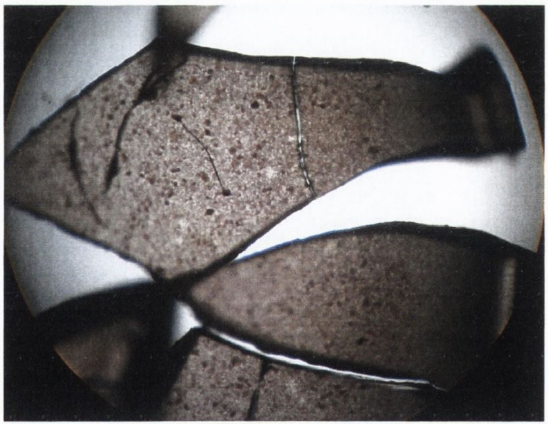
1 Tegovakon+Isopropanol Low content PMC	2 Tegovakon+Isopropanol Low content PMC
	
3 Wacker+Isopropanol Medium content PMC	4 Tegovakon+MEK High content PMC
	

Figure 6.11: Images of cracking in PMC gel plates 4 weeks after preparation (1- isometric view, 2-4- viewed at 20x magnification under compound microscope)

6.3.2 SEM analysis of PMC gel plates

SEM analysis of the PMC gel plates showed the fracture characteristics of the bulk gels. The top surface of the medium particle content gels is quite smooth; however the bottom parts show signs of considerable deformation, perhaps due to the progress of the condensation and effects of agglomeration settling (Figure 6-12, 1). The radiating conchoidal fractures in the cross section demonstrate how the kinetics of the evaporation proceeds, with the arcing lines almost orthogonal to evaporation vectors. The degree of polymerisation is locally important, influencing the propagation of the shrinkage fractures. In places these effects can be seen to be similar to the stress and fracturing of cliff faces, therefore being strongly influenced by orientation.

In the higher particle content gels the frequency of agglomerated particles is evident on the surface (Figure 6-12, 2). The fracture propagation is primarily a function of evaporation and shrinkage. In places it can be seen that higher local particle content sometimes acts as stress concentrators however, with the cracks arcing through regions of higher content. Even the low particle content gels displayed the same agglomeration effects. This highlights the importance of adequate dispersion if these products are to be applied to monuments.

One discrepancy was noted: the composition of the gel plate computed by EDX analysis was shown to have very little Aluminium content, so perhaps the content varied locally, with some parts having a localised concentration of Al due to self-agglomeration.

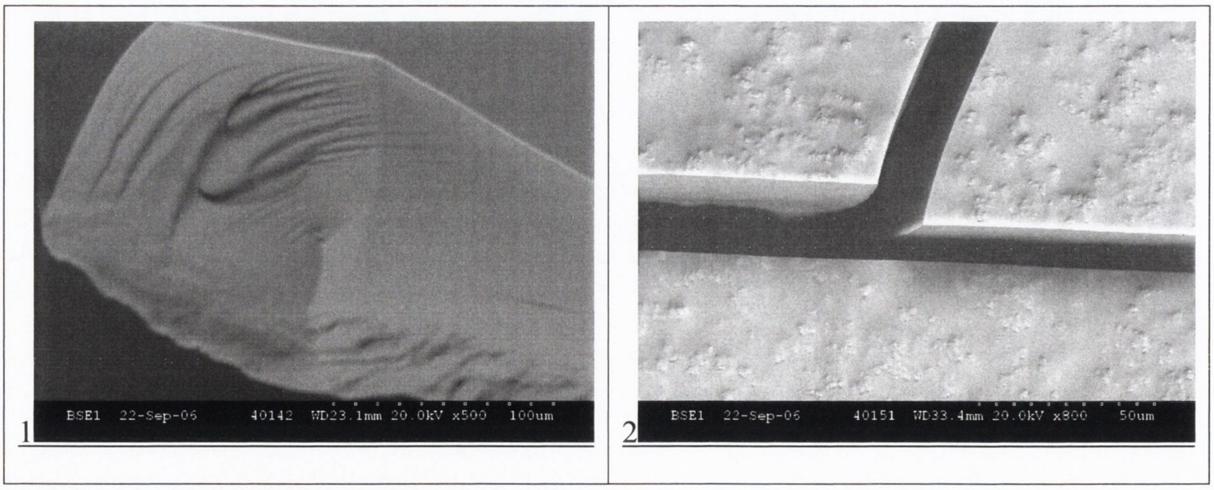
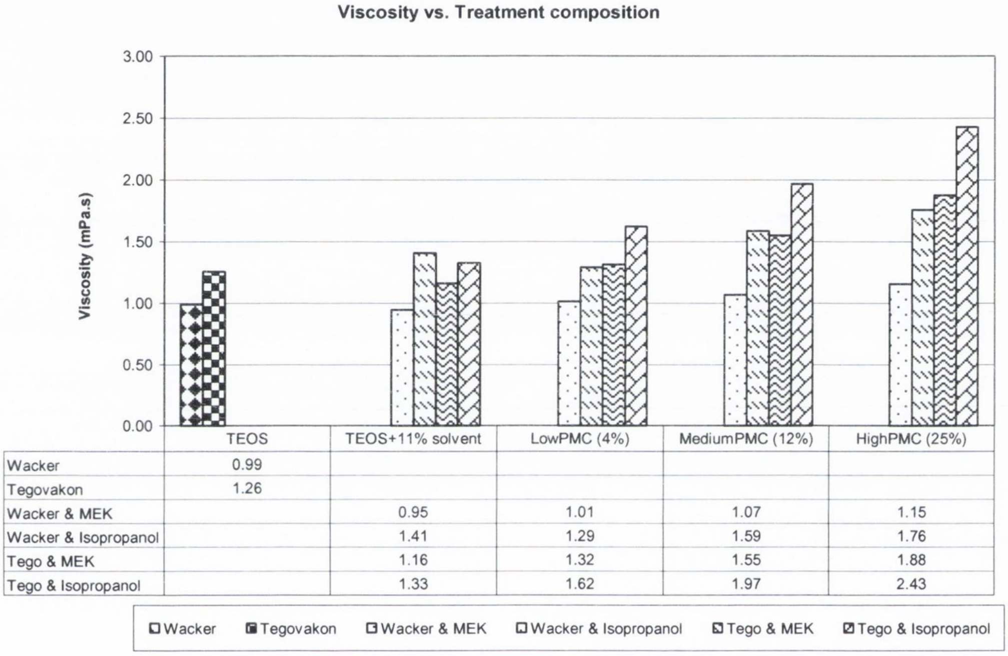


Figure 6.12: Images of PMC gels viewed with SEM

6.3.3 Viscosity of the treatments applied

The viscosity of the treatments used to prepare gels and in consolidating the sandstone samples were measured according to the method described in *Section 5.4.5*.

The viscosity was observed to be reduced slightly by the addition of MEK, but increased slightly by the addition of Isopropanol. Higher particle content also caused the viscosity to increase, as shown in Figure 6-13.



	TEOS	TEOS+11% solvent	LowPMC (4%)	MediumPMC (12%)	HighPMC (25%)
Wacker	0.99				
Tegovakon	1.26				
Wacker & MEK		0.95	1.01	1.07	1.15
Wacker & Isopropanol		1.41	1.29	1.59	1.76
Tego & MEK		1.16	1.32	1.55	1.88
Tego & Isopropanol		1.33	1.62	1.97	2.43

Figure 6.13: Viscosity of the treatment composition according to solvent and particle content

The viscosity of the Wacker treatments was increased from approximately 1.0-1.4 mPa.s to 1.2-1.8 mPa.s by the addition of the nanoparticle content.

The viscosity of the Tegovakon treatments was increased from 1.2-1.4 mPa.s to 1.9-2.4 mPa.s by the addition of the nanoparticle content.

6.3.4 Gelation of consolidant treatments

The evaporation of solvent by-products from the samples during gelation was monitored. Consecutive mass measurements were taken in order to quantify the progress of consolidant condensation, as outlined in *Section 5.4.4*. The percentage shown is the proportion of the total mass of consolidant applied that evaporated in the time since application was completed. This is plotted for the specific products (Wacker in Figure 6-14 and Tegovakon in Figure 6-15). The average evaporation from their respective gel plates is represented by the lines in bold.

Both Wacker and Tegovakon based treatments seem to have profiles characteristic of their compositions. The Wacker proceeds faster, attaining a higher percentage of total evaporation after 7 days. This must be due to the higher degree of polymerisation of the Wacker consolidant, and ensures that the majority of condensation occurs within the first 7-10 days. Tegovakon proceeds more slowly, with condensation processes continuing gradually even up until 60 days after application/preparation. The total evaporation of the Tegovakon was lower than for the Wacker, at 53% compared to 59%. This must be the combined effect of the lower degree of polymerisation and the higher catalyst content in Tegovakon.

These differences between the two products were also observed when applied to the sandstone samples. The principal difference between the evaporation from the gel plates and from the treated samples was the reduction caused by the surface characteristics of the liquid-air interface. The gel plates were simple planar elements and so had different evaporation conditions than the solutions in the treated samples that were lining the pore walls. The rates of evaporation were much lower from the pores, however their progress was observed to have been substantially complete within 3 weeks.

There appeared to be occasional shifts in the rate of evaporation of by-products from the consolidants, particularly when applied to the sandstone samples. This was more noticeable for the Tegovakon treatments and so could be indicative of the availability of monomers and polymers to condense in the gel. This could have an effect on cracking and the ability of the gels to conform within pores in the latter stages of condensation.

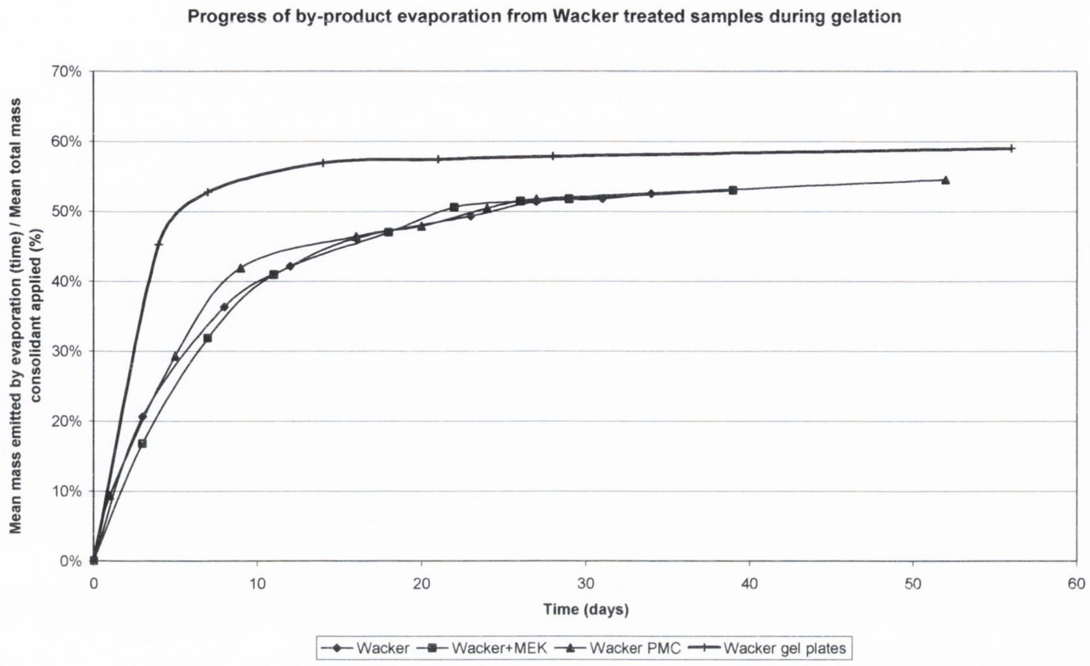


Figure 6.14: Progress of by-product evaporation from Wacker treated samples and gels during condensation

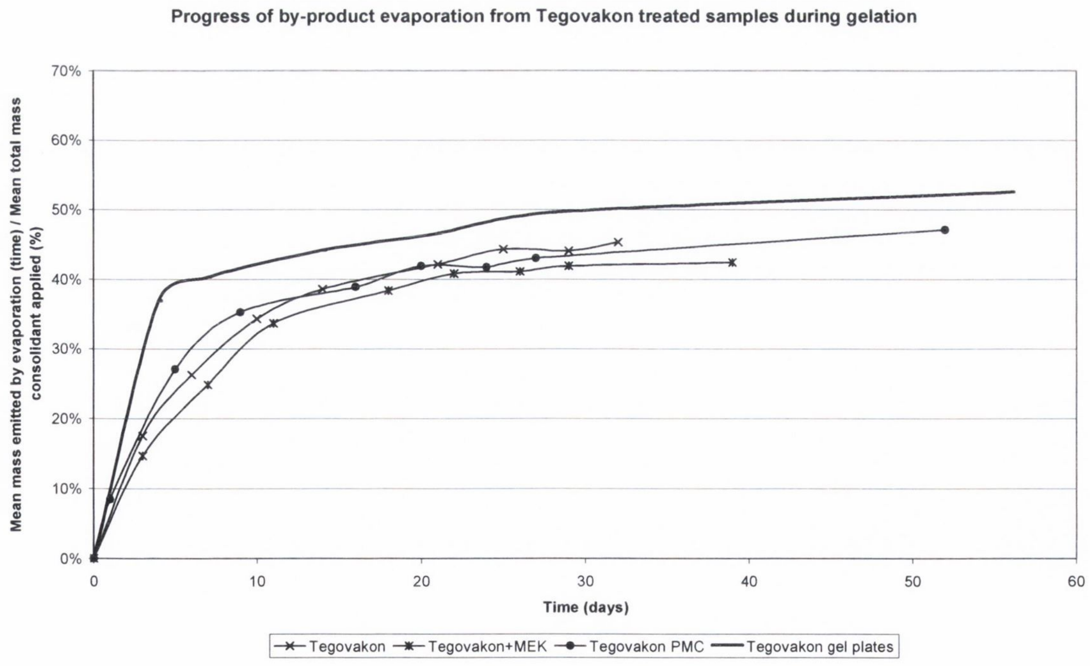


Figure 6.15: Progress of by-product evaporation from Tegovakon treated samples and gels during condensation

6.4 Effects of consolidant treatment on sandstone samples

6.4.1 Properties of consolidated sandstones

The changes in the properties of the samples due to the treatments are very sample-specific. This was mainly due to the increased variability introduced into the samples by continued weathering effects such as fracture propagation or loss of friable material.

6.4.1.1 Changes in mass structure properties due to treatment

The average mass of all sample groups was increased due to consolidant treatment, as shown in Table 6-16. The Drumbane Rusty and Clara Hill samples were changed the most, on average increasing (each cube) in mass by 6.1g and 3.1g respectively. Some of the Killaloe samples gained the least at between 0.3 and 0.5g.

The changes in open porosity were widely varying with some samples displaying net increases and others showing net decreases. It was thought that these increases were due to the gradual propagation of fractures in samples with time, opening up previously closed pores, due to the removal of friable material from the surface, or even because of the removal of salts from some samples. The increases were lower in low porosity samples, ranging from +0.1% for Killaloe buff to +0.2% for Drumbane grey.

The apparent density of all samples increased due to treatment, again with the largest increases occurring in the Drumbane Rusty prisms and Clara Hill Yellow at approximately +29 kg/m^3 and +35 kg/m^3 respectively.

Sample	No. cubes	Cube mass (g)				Open porosity (%)				Apparent density (kg/m^3)			
	W∩T	Weathered		Treated		Weathered		Treated		Weathered		Treated	
Drumbane Grey	20	299.5	279.2 314.7	300.4 *+0.3%*	279.9 315.3	4.1	3.4 4.9	4.4 *+7%*	2.6 6.0	2566	2524 2588	2562 *-0.1%*	2518 2593
Drumbane Rusty (Cubes)	10	266.3	244.6 274.8	267.4 *+0.4%*	245.1 276.7	8.6	7.6 9	10.8 *+26%*	6.2 11.5	2355	2322 2375	2384 *+1.2%*	2341 2405
Drumbane Rusty (Prisms)	11	349.1	310.4 378.4	355.2 *+1.7%*	324.1 381.0	13.0	11.6 14.5	12.7 *-2%*	8.5 16.0	2241	2206 2263	2270 *+1.3%*	2237 2297
Manorhamilton	30	282.7	244.1 323.8	285.2 *+0.9%*	245.9 280.9	11.6	9.1 13.2	9.3 *-20%*	5.8 11.5	2314	2275 2346	2336 *+1.0%*	2287 2370
Clara Hill Grey	19	320.1	270.9 360.4	318.5 *-0.5%*	274.1 361.9	6.4	3.2 9.7	5.8 *-9%*	4.7 7.9	2481	2404 2488	2492 *+0.4%*	2204 2492
Clara Hill Yellow	12	268.2	219.6 327.6	271.3 *+1.1%*	221.5 326.2	16.4	9.2 19.5	15.2 *-7%*	11.7 19.5	2168	2081 2320	2203 *+1.6%*	2129 2316
Killaloe Buff	12	373.1	340.0 427.4	373.4 *+0.1%*	340.4 427.8	2.1	1.8 2.3	1.9 *-10%*	1.2 3.4	2551	2531 2568	2550 -0.4%	2532 2572
Killaloe Grey-Green	11	366.8	350.0 375.7	367.2 *+0.1%*	350.3 376.3	1.4	1.2 1.7	2.4 *+71%*	0.5 3.1	2661	2632 2701	2662 *+0.4%*	2633 2699
Killaloe Ochre	4	333.9	325.1 344.9	334.4 *+0.1%*	325.5 345.4	1.9	1.7 2.2	2.8 *+47%*	0.9 3.6	2545	2528 2554	2546 *+0.4%*	2533 2557
Killaloe Dark Grey	6	357.2	327.6 403.8	358.8 *+0.4%*	329.6 404.3	6.5	1.5 9.6	6.2 *+5%*	1.6 10.4	2442	2318 2634	2450 *+0.3%*	1330 2639

Table 6-16: Comparison of mass structure properties of weathered (W) and treated (T) sandstone samples (mean, minimum and maximum values)

6.4.1.1.1 Gain in mass per unit area due to treatment

The average gain in mass of each sandstone sample as a result of the applied treatments is shown in Table 6-17, alongside the average open porosity of the relevant samples. These are shown individually for each of the treatment types in the following figures, Figures 6.16-18:

Mass gain per unit area of application surface (g/m^2), and open porosity of respective samples (%)							
Product applied Sample	Wacker	Wacker +MEK	Wacker PMC	Tegovakon	Tegovakon +MEK	Tegovakon PMC	Average
Drumbane Grey	690 4.3%	448 4.2%	283 3.7%	274 4.1%	299 4.0%	241 3.9%	373 4.0%
Drumbane Rusty (Cubes)	711 8.7%	428 8.0%	257 9.0%	423 8.6%	412 8.2%	444 9.2%	446 8.6%
Drumbane Rusty (Prisms)	1116 13.8%	1387 13.2%	769 13.7%	731 12.4%	1504 11.9%	853 12.2%	1060 12.9%
Manorhamilton	1517 11.7%	1691 11.5%	730 12.4%	841 11.2%	1079 11.3%	717 11.4%	1096 11.6%
Clara Hill Grey	859 6.6%	743 5.6%	729 6.5%	539 6.2%	604 6.4%	1468 8.0%	824 6.6%
Clara Hill Yellow	1470 13.5%	1398 16.8%	864 17.0%	1392 18.5%	1320 16.8%	1487 15.9%	1322 16.4%
Killaloe Buff	153 2.1%	154 2.0%	149 2.2%	69 2.2%	83 2.2%	90 2.1%	116 2.1%
Killaloe Grey/Green	214 1.3%	124 1.2%	118 1.3%	63 1.7%	128 1.5%	141 1.5%	131 1.4%
Killaloe Ochre	267 1.7%	187 1.9%	- -	173 1.5%	150 1.8%	- -	194 1.7%
Killaloe Dark Grey	742 8.4%	175 1.5%	630 8.0%	605 6.2%	199 5.4%	686 9.6%	506 6.5%
Average	774 8.0%	674 7.3%	503 8.7%	511 7.7%	578 6.7%	681 8.6%	699 7.8%

Table 6-17: Gain in sample mass per unit area of application surface due to each consolidant treatment

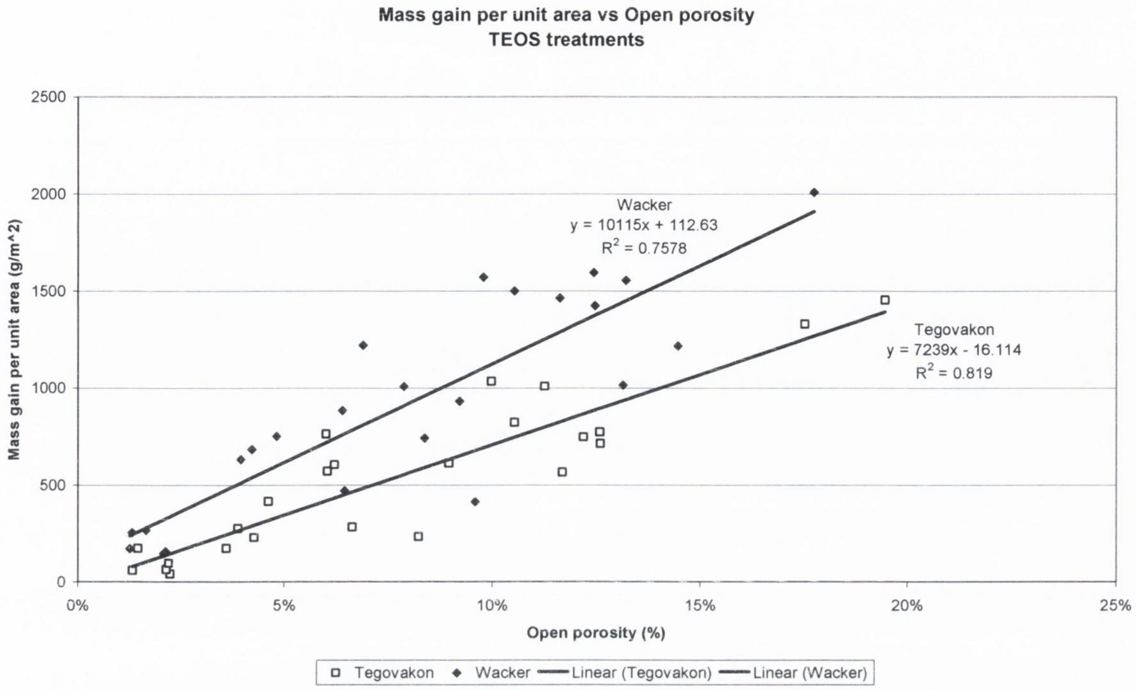


Figure 6.16: Comparison of specific mass gain vs. open porosity for samples treated with TEOS consolidant treatments

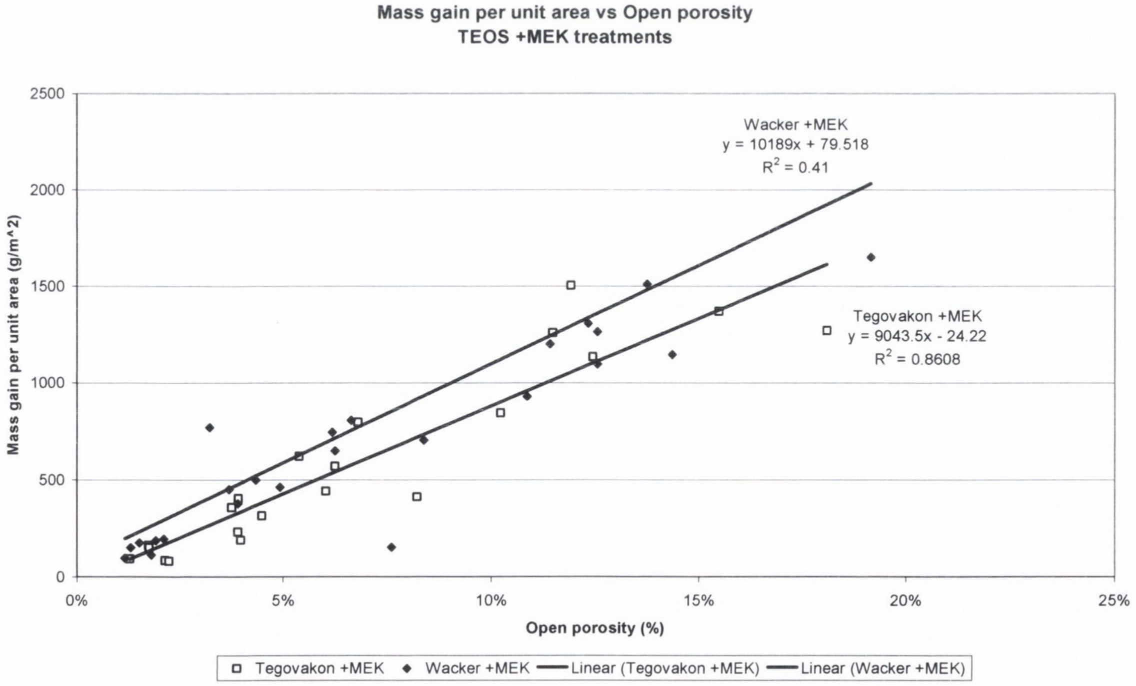


Figure 6.17: Comparison of specific mass gain vs. open porosity for samples treated with TEOS +MEK solvent treatments

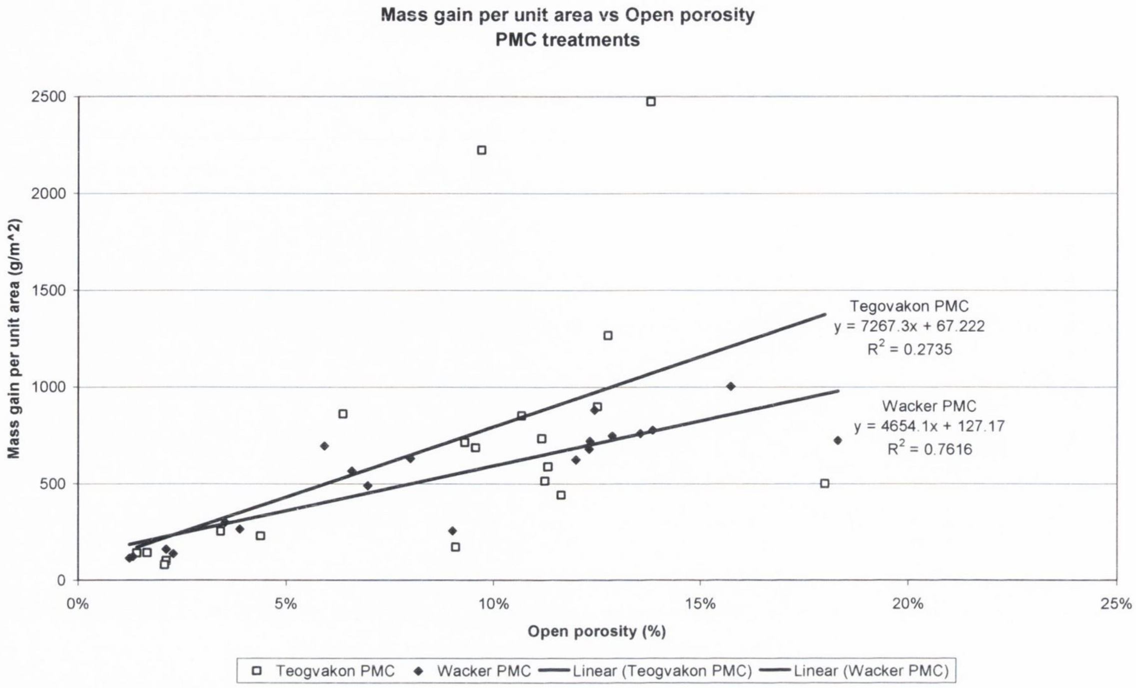


Figure 6.18: Comparison of specific mass gain vs. open porosity for samples treated with PMC treatments

Comparing the average values of mass gain per unit area for the different treatments in Table 6-17 does not show any significant relationship.

From Figures 6-16 to 6-18 it can be seen that the Wacker product achieved slightly better results compared to the Tegovakon products when used on its own or with solvent content. For the PMC treatment it is observed that the Tegovakon PMC achieved better results, primarily because of 2 outliers. The variation in the Tegovakon PMC treated samples was very high compared to those for other treatments.

6.4.1.2 Changes in moisture transfer properties due to treatment

6.4.1.2.1 Capillary absorption

The values for the capillary absorption of the treated samples are presented in Table 6-18 on the next page.

Most of the samples' capillary absorption rates were reduced, presumably due to the changes in mass structure and porosity characteristics. The capillary absorption coefficients of the Manorhamilton samples were increased however. By comparison with the values calculated for the later time periods it is seen that the treatment has had an inflected effect on them; the initial absorption (coefficient) and long term absorption (2nd

24 hours) are higher, yet medium term absorption (1st 24 hours) is lower. This echoes the inversion of the capillary absorption rates mentioned in *Section 6.2.3.2.* Changes to the pores either increase early capillary absorption, directly reducing the amount likely to occur subsequently, or vice versa.

Sample	No. cubes	Coefficient (g/m^2/s$^{1/2}$)				1st 24 hours (g/m^2/s$^{1/2}$)				2nd 24 hours (g/m^2/s$^{1/2}$)			
	Wn T	Weathered		Treated		Weathered		Treated		Weathered		Treated	
Drumbane Grey	20	11.5	4.4 15.8	8.5 *-26%*	1.7 13.8	5.0	3.3 7.8	3.8 *-24%*	1.5 6.5	1.3	0.1 2.6	1.9 *+46%*	0.4 3.2
Drumbane Rusty (Cubes)	10	42.2	8.9 57.7	10.2 *-76%*	2.6 31.6	9.5	6.2 11.5	9.6 *+11%*	2.6 12.1	2.4	0.3 4.6	1.7 *+29%*	0.7 3.7
Drumbane Rusty (Prisms)	11	50.9	22.8 77.7	24.0 *-53%*	6.5 37.5	13.3	10.6 17.4	9.4 *-29%*	3.9 15.3	1.0	0.4 3.6	2.7 *+170%*	0.7 5.9
Manorhamilton	30	9.5	6.8 66.9	11.6 *+22%*	8.3 28.9	9.0	2.8 12.6	6.5 *-28%*	2.8 9.6	2.5	0.4 12.6	3.0 *+20%*	0.1 5.9
Clara Hill Grey	19	31.1	7.6 63.5	26.9 *-14%*	7.0 45.8	7.8	6.2 8.7	6.9 *-11%*	4.8 8.1	3.0	0.3 9.0	1.5 *-50%*	0.1 4.5
Clara Hill Yellow	12	38.1	25.8 57.5	36.7 *-4%*	17.0 67.9	11.6	7.5 16.2	8.8 *-24%*	5.8 15.6	2.6	0.9 5.9	2.6 *0%*	1.3 3.3
Killaloe Buff	12	2.1	1.0 4.1	1.5 *-29%*	0.7 2.7	2.7	2.1 3.3	1.6 *-41%*	0.8 2.6	1.7	0.6 2.1	0.6 *-65%*	0.2 2.2
Killaloe Grey/Green	11	3.0	1.9 6.5	1.9 *-37%*	1.3 2.5	1.6	1.3 2.3	1.2 *-25%*	0.8 2.4	0.4	0.2 0.6	0.6 *+50%*	0.3 1.1
Killaloe Ochre	4	3.7	1.9 7.2	3.7 *0%*	1.5 6.5	2.4	2.1 2.7	1.5 *-38%*	0.7 1.9	0.9	0.5 1.3	0.2 *-78%*	0.0 0.4
Killaloe Dark Grey	6	16.2	5.7 22.7	16.6 *+2%*	4.4 31.3	4.9	1.4 6.9	4.4 *-10%*	1.1 9.2	1.7	0.1 7.1	1.5 *-12%*	0.3 3.9

Table 6-18: Comparison of capillary absorption rates in weathered (W) and treated (T) sandstone samples (mean, minimum and maximum values)

6.4.1.2.2 Evaporation

The values for the evaporation rates of the treated samples are presented in Table 6-19.

The changes in the evaporation differed considerably: decreases were prevalent in the Drumbane Grey, Manorhamilton and Clara Hill samples, while little or no change was recorded in the Drumbane Rusty samples. The increases observed in most of the Killaloe samples were perhaps due to increases in the diffusive ability of moisture from within the stone through smaller pores to the surface environment.

Sample	No. cubes	1st 24 hours ($g/m^2/s^{½}$)				2nd 24 hours ($g/m^2/s^{½}$)			
	Wn T	Weathered		Treated		Weathered		Treated	
Drumbane Grey	20	40	26 57	28 *-30%*	14 55	12	9 19	17 *+42%*	8 27
Drumbane Rusty (Cubes)	10	87	73 100	42 *-52%*	19 57	23	19 29	20 *-13%*	12 30
Drumbane Rusty (Prisms)	11	66	59 74	60 *-9%*	40 71	67	58 80	27 *-60%*	17 38
Manorhamilton	30	60	49 82	72 *+20%*	28 118	57	20 79	33 *-42%*	13 64
Clara Hill Grey	19	56	18 75	43 *-23%*	29 73	23	16 53	15 *-35%*	7 26
Clara Hill Yellow	12	66	41 93	78 *+18%*	62 104	50	12 89	50 *0%*	17 108
Killaloe Buff	12	25	22 29	16 *-36%*	12 22	8	6 11	10 *+25%*	5 15
Killaloe Grey/Green	11	13	10 17	20 *+54%*	10 51	4	3 7	8 *+50%*	5 20
Killaloe Ochre	4	24	21 27	26 *+8%*	15 39	7	6 7	12 *+71%*	5 14
Killaloe Dark Grey	6	65	15 102	76 *+172%*	28 105	24	5 45	45 *+88%*	11 74

Table 6-19: Comparison of evaporation rates of weathered (W) and treated (T) sandstone samples (mean, minimum and maximum values)

6.4.1.3 Comparison of mechanical strength of weathered and treated samples

The numbers of samples tested for mechanical strength was limited because many featured inappropriate dimensions due to the material losses caused by artificial weathering. For this reason the samples tested were probably the most durable of the sample groups, whether treated or not, and the results are statistically poor.

The apparent density and modulus of elasticity of weathered and treated samples are compared in Table 6-20 on the next page. Comparisons of the modulus of elasticity and compressive strength calculated by loading and stress/strain analysis are shown in Table 6-21 on the page after.

Sample		PUNDIT				
	W/T	No. cubes	Apparent density (kg/m^3)		Modulus of elasticity (GPa)	
Drumbane Grey	W	2	2569	2560 2577	31	30 31
	T	4	2572	2543 2589	35	30 43
Drumbane Rusty	W	1	2244	- -	12	- -
	T	2	2289	2284 2294	21	20 22
Manorhamilton	W	2	2321	2317 2326	21	21 21
	T	9	2342	2327 2357	28	20 34
Clara Hill Grey	W	0	-	- -	-	- -
	T	3	2462	2452 2483	22	18 26
Clara Hill Yellow	W	0	-	- -	-	- -
	T	1	2131	- -	22	- -
Killaloe Buff	W	1	2552	- -	43	- -
	T	4	2556	2550 2572	41	32 48
Killaloe Grey-Green	W	0	-	- -	-	- -
	T	8	2661	2633 2699	43	35 53
Killaloe Ochre	W	0	-	- -	-	- -
	T	1	2557	- -	39	- -
Killaloe Dark Grey	W	0	-	- -	-	- -
	T	2	2496	2354 2639	43	31 54

Table 6-20: The modulus of elasticity of weathered (W) and treated (T) samples calculated using the PUNDIT apparatus (also shown are the number and apparent density of cubes tested)

Sample	W/T	No. cubes	Apparent density (kg/m^3)		Modulus (GPa)		Compressive strength (N/mm^2)	
Drumbane Grey	W	1	2560	2560	32	-	97	-
				2577		-		-
	T	1	2543	2543	34	-	121	-
				2589		-		-
Drumbane Rusty	W	0	-	-	-	-	-	-
				-		-		-
	T	0	-	-	-	-	-	-
				-		-		-
Manorhamilton	W	2	2321	2317	30	30	41	29
				2326		31		53
	T	2	2328	2327	42	31	57	30
				2329		52		84
Clara Hill Grey	W	0	-	-	-	-	-	-
				-		-		-
	T	0	-	-	-	-	-	-
				-		-		-
Clara Hill Yellow	W	0	-	-	-	-	-	-
				-		-		-
	T	0	-	-	-	-	-	-
				-		-		-
Killaloe Buff	W	1	2542	-	43	-	100	-
				-		-		-
	T	1	2556	-	38	-	94	-
				-		-		-
Killaloe Grey-Green	W	1	2636	-	33	-	140	-
				-		-		-
	T	3	2654	2633	40	39	153	122
				2669		41		175
Killaloe Ochre	W	0	-	-	-	-	-	-
				-		-		-
	T	1	2557	-	39	-	-	-
				-		-		-
Killaloe Dark Grey	W	0	-	-	-	-	-	-
				-		-		-
	T	2	2496	2354	43	31	-	-
				2639		54		-

Table 6-21: The modulus of elasticity and compressive strength for weathered (W) and treated (T) samples, calculated by loading to crushing (also shown are the number and apparent density of the cubes tested)

6.4.1.3.1 Drumbane

Only 1 cube of weathered Drumbane Grey sandstone was available for crushing. The data obtained suggested that weathering had reduced compressive strength by 24% from 121 N/mm^2 to 97 N/mm^2. The PUNDIT apparatus suggested that its modulus was 31 GPa, close to the value of 32 GPa calculated by stress/strain analysis. This was a reduction of approximately 35% from the 42 GPa obtained by loading for the unweathered samples (*Section 6.1.4*).

Measurements on the treated cubes with the PUNDIT suggested an average modulus of 36 GPa, 15% lower than the unweathered value and 16% greater than the weathered value mentioned above. Similarly only one cube of treated Drumbane Grey sandstone was suitable for crushing. Its compressive strength was practically unchanged from the unweathered value at 121 N/mm^2, while its modulus was 34 GPa, 19% lower than the unweathered value but 8% greater than the weathered (but untreated) one.

No cubes of the weathered Drumbane Rusty samples were suitable for crushing. Its modulus was determined to be 12 GPa from measurements taken with the PUNDIT apparatus, although this was on a slightly fractured Prism. This was a reduction of 52% when compared with a similar sample that had been crushed to determine the unweathered properties. Comparable samples that were treated were determined to have values of approximately 21 GPa, 18% lower than the unweathered value but 78% greater than that determined for the weathered (but untreated) sample. While it is not likely that the consolidant treatment increased modulus from 12 GPa up to 21 GPa, it is likely that it contributed some amount to the higher density (to which the square of the measured velocity is correlated to calculate the modulus). Based on the increases of between 20 and 35 kg/m^3 in apparent density shown in Table 6-15 above, the contribution is at least in the range of 0.8 to 1.6%.

The great difference between the unweathered and weathered values may exacerbate the distinctions between the Grey and Rusty types. Their strength may thus vary considerably with weathering, in addition to their appearances.

6.4.1.3.2 Manorhamilton

The PUNDIT apparatus suggested a value for modulus of elasticity of 21 GPa, obtained on two weathered (but untreated) cubes. This was lower than the value obtained by stress/strain analysis during loading. The same two cubes were both determined by stress/strain analysis to have a modulus of elasticity of 30 GPa.

One cube failed at a compressive strength of 29 N/mm^2, approximately 28% of the mean unweathered strength of 105 N/mm^2. This was seen to have a brittle shear mode of failure with planar rather than conical features. The other one had a compressive strength of 53 N/mm^2, approximately 51% of this unweathered value.

Two comparable treated cubes were determined to have a modulus of 42 GPa, 15% higher than the modulus obtained for the unweathered cubes by crushing. One of these was also seen to fail in a brittle manner however, having a modulus of 52 GPa, over 40% higher than that of the unweathered samples. Its appearance was altered by mineral discolouration to a dark black due to dissociation of iron oxides. These may have altered the cements in the sample thus raising the modulus but reducing the strength. The other cube was seen to have a modulus of 31 GPa, 14% lower than the unweathered value, but only 3% higher than the weathered (untreated) samples'.

Reduced compressive strength and brittle elastic failure may occur in weathered samples. Treatment with consolidants may increase the modulus of elasticity.

6.4.1.3.3 Clara Hill

No samples of the weathered or treated Clara Hill sandstone were suitable for crushing; however measurements were made on several treated samples with the PUNDIT apparatus. The modulus of both the Grey and Yellow types were within the same range, and taken to be 22 GPa, 26% and 74% greater than the estimated values for the unweathered Grey and Yellow samples respectively.

The Clara Hill sandstone may become more brittle locally due to the variation in the modulus of elasticity.

6.4.1.3.4 Killaloe

The number of weathered (but untreated) and treated cubes suitable for crushing was low. PUNDIT measurements on the weathered cubes showed the Buff sample to have a modulus of 43 GPa, while for the Grey-Green one it was 41 GPa. This represents a 1% reduction in the Buff, and a 28% increase in the Grey-Green. Their compressive strengths were 100 N/mm^2 and 140 N/mm^2, 24% lower and 31% higher than their unweathered values respectively.

The value obtained by the PUNDIT apparatus on the treated Buff samples was 41 GPa, 8% lower than the unweathered value but also 2% lower than the weathered values. One of the cubes was attached to two strain gauges during crushing, one on the treated surface, and one on the untreated reverse surface. The modulus of each was calculated: for the untreated surface it was 33 GPa, while for the treated it was 40 GPa, 20% higher.

The variability in the compressive strength of the weathered and treated samples may cause concern for the stability of Killaloe stone in monuments. The data suggests that treating weathered surfaces with consolidants should refresh the elastic properties of the stone to some degree, depending on their condition.

6.4.2 Tests to measure depth of penetration

The tests for the depth of penetration of the consolidant into the sandstones from the application surface were carried out as described in the *Chapter 5: Methods and Materials*. The water drop absorption rates of the samples were determined and surface wetting effects observed. In several instances the presence of consolidant could be seen, especially where the PMC treatment had been applied.

6.4.2.1 Water drop absorption test

This method assumed that the time taken to absorb the water droplet was somewhat higher if consolidant was present and therefore reducing the available pore space. The readings obtained were analysed to highlight the presence of the consolidant at certain depths, which were then split in proportion to the frequency of occurrences (see Table 6-22 on the next page). The averages of all values obtained are presented in the table.

Indeterminate cases were encountered where the values showed higher absorption times in the inner parts of the samples than in parts of the sample near the application surface. This could be true in the case of more highly weathered sandstone where porosity is still greater in outer parts despite the presence of consolidant, for example. Assuming that this would be true in some, but not all cases, the range of results obtained are shown alongside the percentage of readings on which the values are based. For example, a reading using 80% of the results obtained indicates that 1 reading in 5 was in some way indeterminable. Ignoring these indeterminate cases on the assumption that the outer areas are weathered but successfully treated, the reading would have been 100%.

Other indeterminate cases were also encountered, such as those where absorption times were higher, lower and then higher again, presumably due to varying composition or negligible differences between readings.

Sample	No. of cubes read	Depth of penetration (mm), and percentage of determinable readings					
		Average		Minimum		Maximum	
Drumbane Grey	15	11.0	73%	9.1	63%	14.7	79%
Drumbane Rusty	10	11.2	82%	10.0	65%	12.3	91%
Manorhamilton	11	12.0	81%	10.5	62%	13.9	91%
Clara Hill Grey	10	9.7	37%	5.0	20%	14.4	53%
Clara Hill Yellow	4	11.3	63%	10.0	60%	12.5	67%
Killaloe Buff	7	8.2	84%	5.0	67%	12.9	100%
Killaloe Grey-Green	4	7.4	92%	5.0	75%	12.2	100%
Killaloe Ochre	3	13.3	89%	12.5	67%	15.0	100%
Killaloe Dark Grey	3	12.0	50%	5.0	33%	16.0	60%

Table 6-22: Depth of penetration calculated by the Water drop absorption test showing both average and range of values calculated for the sandstone samples and the percentage of the total number of readings they were determined on

The results presented here are very simplistic, yet they provide an insight to the depths of penetration achieved in the samples. Effectively the results are a function of the spacings used in the tests, so experimental parameters had a direct influence on the results.

It was difficult to reduce the spacings in order to increase the spread of readings and lower the corresponding errors. This was mainly because of the increased timing requirements. In some of the more porous samples the drops also spread out, infringing on the absorption of adjacent drops. The repeatability of the test was low because of these problems and results based on small sample groups were more susceptible to bias.

The accuracy of these results is questionable when several of the main findings are compared. For instance, the range of values determined for both the Clara Hill Grey and Killaloe Dark Grey samples is very wide (5.0 to 14.4mm, and 5.0 to 16.0mm respectively), based on a relatively low proportion of cubes. The lower levels of accuracy leave much greater possibility for more extreme range of results. Consequently, the results of this test require verification by complementary methods.

The results were also analysed from the point of view of the depths of penetration achieved by each treatment, as shown in Table 6-23:

Sample	No. of cubes read	Depth of penetration (mm), and percentage of determinable readings					
		Average		Minimum		Maximum	
Wacker	10	10.1	82%	9.2	78%	10.7	86%
Wacker +MEK	6	11.4	85%	9.1	83%	12.5	86%
Wacker PMC	13	10.5	82%	8.5	76%	11.8	85%
Tegovakon	7	10.9	90%	10.4	86%	11.3	93%
Tegovakon +MEK	13	9.2	80%	8.5	69%	10.5	100%
Tegovakon PMC	12	10.4	79%	8.8	75%	11.4	84%

Table 6-23: Depth of penetration calculated by the Water drop absorption test showing both the average and range of values calculated when arranged by treatment type, and the percentage of the total number of readings they were determined on

These results are not directly comparable with each other. Treatments with MEK were applied to samples that were less affected by the weathering, while PMC treatments were applied to samples that had been more affected by the weathering. The results obtained on the PMC treated samples are very similar for both products. The other results are more highly varied, presumably due to individual sample conditions.

6.4.2.2 Surface wetting test

The results of the surface wetting test were very useful, in that they clearly showed a dividing line between rates of drying/absorption. The effects were repeatable and can be wholly attributed to the presence of consolidants to that depth in most cases. Where the dry/wet line varies in depth profile, a range of the depths were reported, however in a minority of cases the depth was uniform and a single value given. In verifying the test 3 untreated cubes were included and they displayed no effects whatsoever.

The readings obtained were relatively moderate, neither too low nor too high. The method was repeatable and gave greater insight on the inner structure of the cubes. The depth at which salt crystallisation occurred during weathering was evident in some samples: particularly those that became fractured. It was clear that in most cases the consolidant had penetrated into the stone at least as far as the drying line on the side nearest the application surface.

The sampling and results obtained are presented in Table 6-24 on the next page, arranged in a matrix of the sandstone samples and treatment products.

Depth of Penetration (mm) (readings by Surface wetting test)							
Product applied Sample	Wacker	Wacker +MEK	Wacker PMC	Tegovakon	Tegovakon +MEK	Tegovakon PMC	Range
Drumbane Grey	11,13	-	11	-	11	-	[11,13]
Drumbane Rusty	11	17,10	8	6,8	5,10	5,18	[5,18]
Manorhamilton	30	-	23, 6, 16	22	17	17,23	[6,30]
Clara Hill Grey	7	9,10,20	8,20	-	7,20	6,8	[6,20]
Clara Hill Yellow	11,12	-	-	-	13	13	[11,13]
Killaloe Buff	-	11	17,18	7	11	18	[7,18]
Killaloe Grey/Green	20	-	-	-	-	12	[12,20]
Killaloe Ochre	13	8	-	8	-	-	[8,13]
Killaloe Dark Grey	-	-	-	-	-	-	-
Range	[7,30]	[8,20]	[6,23]	[6,22]	[5,20]	[5,23]	-

Table 6-24: Range of values obtained for the depth of penetration using the Surface wetting test according to stone sample and consolidant treatment

These results seem to show that the Wacker products achieved slightly higher penetrations. Ignoring the higher value of 30mm observed in the Manorhamilton/Wacker sample, the maxima observed are almost identical for each, irrespective of which sandstone it was. The minima observed for the Wacker products are 1-3mm higher than for the Tegovakon, however it should be highlighted that these were on a variety of sandstone samples. What seemed to achieve higher penetration on one stone may have performed poorly on another.

The range of results reported for the Surface wetting test is much larger than the range seen for the Water drop absorption test. This is because the former is a scattered list of values, based on visual observation and perception, and the latter is effectively an average value, calculated according to a more scientific framework. From this viewpoint the two tests are complementary, akin to stating both an average result and range of minimum and maximum values. The results are combined for both the sandstone samples and consolidant treatments in Table 6-25 and Table 6-26 respectively:

Sample	Depth of penetration (mm)								
	Water drop absorption			Surface wetting			Combined result		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Drumbane Grey	11	9	15	12	11	13	12	9	15
Drumbane Rusty	11	10	12	10	5	18	11	5	18
Manorhamilton	12	11	14	19	6	30	16	6	30
Clara Hill Grey	10	5	14	12	6	20	11	5	20
Clara Hill Yellow	11	10	13	10	11	13	11	10	13
Killaloe Buff	8	5	13	14	7	18	11	5	18
Killaloe Grey-Green	7	5	12	16	12	20	12	5	20
Killaloe Ochre	13	13	15	10	8	13	12	8	13
Killaloe Dark Grey	12	5	16	-	-	-	12	5	16

Table 6-25: Combined mean, minimum and maximum values obtained using the Water drop absorption test and the Surface wetting test to calculate the Depth of Penetration in the sandstone samples

Sample	Depth of penetration (mm)								
	Water drop absorption			Surface wetting			Combined result		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Wacker	10	9	11	14	7	30	12	7	30
Wacker +MEK	11	9	13	12	8	20	12	8	20
Wacker PMC	11	9	12	13	6	23	12	6	23
Tegovakon	11	10	11	10	6	22	11	6	22
Tegovakon +MEK	9	9	11	12	5	20	11	5	20
Tegovakon PMC	10	9	11	13	5	23	12	5	23

Table 6-26: Combined mean, minimum and maximum values obtained using the Water drop absorption test and the Surface wetting test to calculate the Depth of Penetration achieved using the consolidant treatments

The most likely depth of penetration achievable is between 11mm and 12mm, whether the treatment is modified or not. It may be as low as 5mm, or as high as 30mm.

6.4.3 Observations on treated samples with the Scanning Electron Microscope

On inspection with the SEM the aggregation and cracking of the PMC gel on the surface of the samples were observed. Images at several magnifications were taken of the gel in different parts of the rough surface. It was seen that the shrinkage and curling resembled the dessicated features that occur in dried mud flats, confirming the importance of the evaporation process on the resultant gel (Figure 6-19, 1). On coarser sandstone samples, such as Clara Hill yellow, the PMC gels were less agglomerated and the gels were thinner, spreading more evenly over the surface (Figure 6-19, 2).

The other samples analysed did not show any visible attributes relevant to consolidation. This was due to the preparation of some samples by cutting.

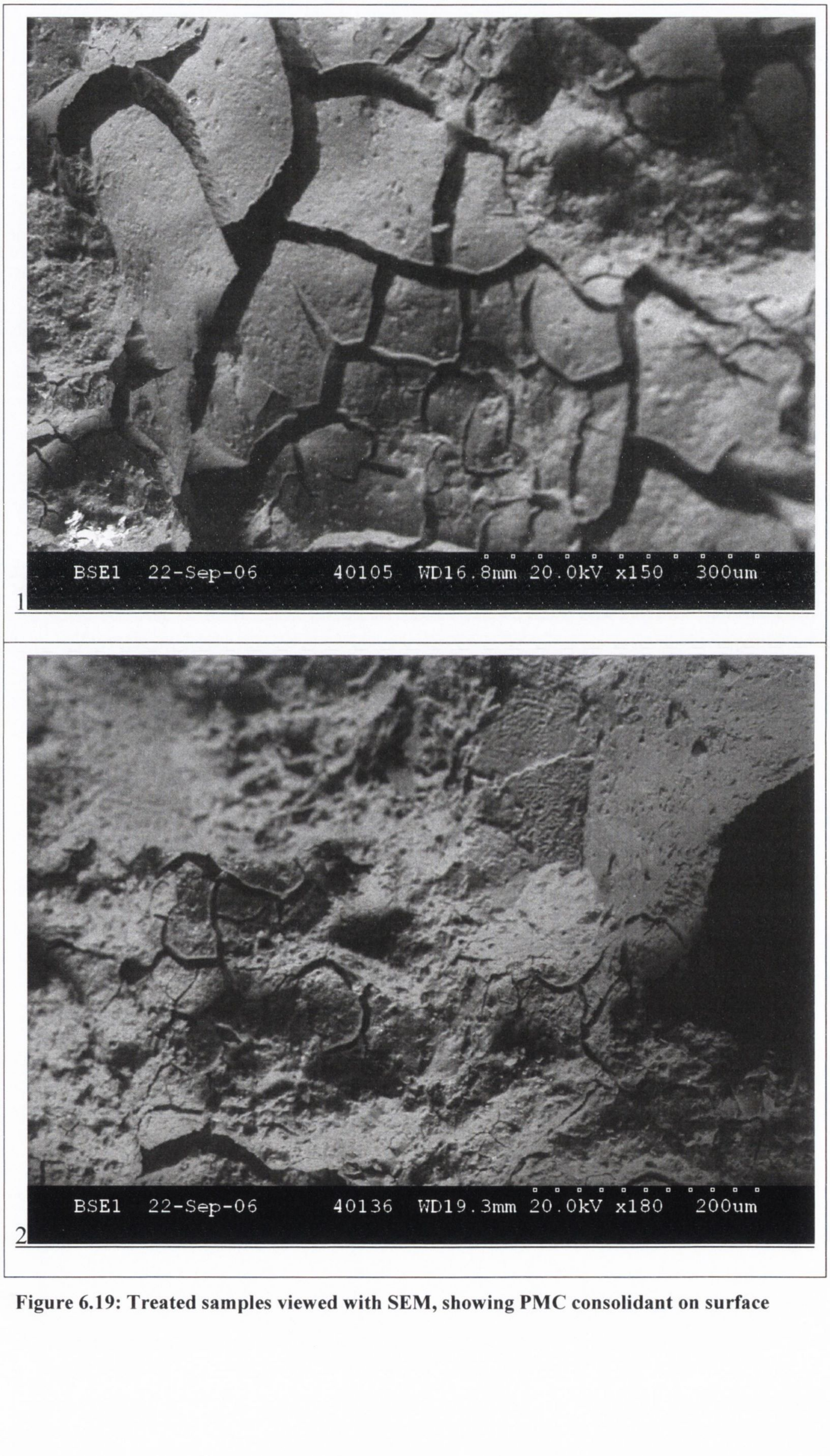


Figure 6.19: Treated samples viewed with SEM, showing PMC consolidant on surface

6.4.4 Comparison of durability of treated and untreated samples

6.4.4.1 Effect of further weathering on mass structure of treated and untreated sandstone

The treated and weathered (untreated) samples were subjected to another 15 cycles of salt weathering to compare their respective durability's. The decay mechanisms seen previously were observed to recur, deteriorating the samples further. The mass losses per unit area of treated and untreated samples are compared in Table 6-27:

Sample	Mass loss per square metre surface (g/m^2)								Ratio (W:T)
	Weathered				Treated				
	No. cubes	Mean	Minimum	Maximum	No. cubes	Mean	Minimum	Maximum	
Drumbane Grey	3	539	232	787	19	112	-105	689	4.8
Drumbane Rusty (Cubes)	1	1583	-	-	4	295	61	850	5.4
Drumbane Rusty (Prisms)	3	9500	8458	10175	10	1430	483	3608	6.6
Manorhamilton	6	665	332	1030	26	139	0	268	4.8
Clara Hill Grey	4	2861	1875	3489	9	530	110	1370	5.4
Clara Hill Yellow	3	1322	501	2473	9	779	195	1580	3.8
Killaloe Buff	2	-39	-91	14	8	-62	-81	-43	0.6
Killaloe Grey-Green	2	0	-3	2	8	-11	-14	-8	0
Killaloe Ochre	1	-13	-	-	3	90	38	150	-0.1
Killaloe Dark Grey	0	-	-	-	3	283	225	321	-

Table 6-27: Ratio of mass loss per unit area of untreated to treated samples when subjected to further weathering (note: negative values indicate gain in mass due to salt accumulating in pores)

In samples of low porosity the mass increased or maintained a net equilibrium due to the additional salt content, with little or no losses. This happened in most of the Killaloe, and some of the treated Drumbane Grey samples. In the medium and high porosity samples, the mass losses were greater in the untreated samples than in the treated ones, by factors greater than 3.8. This indicated that the treatments were successful in protecting the stone from further weathering.

6.4.4.2 Observations on the effects of consolidants on further weathering in cut cross sections

The treated cross sections that were analysed for the depth of penetration analysis were also subjected to further weathering. Mass losses became apparent in all samples. Differences in material loss occurred close to the extents of consolidant penetration, thereby allowing the depth of penetration achieved by the treatments to be measured.

The differences in weathering due to consolidant penetration were primarily evident in the Manorhamilton and Drumbane Rusty samples (e.g., Figure 6-20). The treated Manorhamilton sample in Figure 6-20 (1) has less flaking from the left hand side of the cross section near the surface to which treatment was applied. The consolidant also seemed to achieve greater penetration at the bottom and top, and along the band of different composition in the middle.

The colour of the Drumbane Rusty Prism in Figure 6-20 (2) is slightly darker near the surface to which consolidant was applied. The outer 2-3mm around the entire surface is darker due to weathering exposing ferruginous material, as discussed previously in *Section 6.1.1.1*. Another less perceptible darkness is also present beneath the surface to which consolidant was applied, as noted in the figure.

The Drumbane Rusty Prism in Figure 6-20 (3) had been treated with PMC which blocked the pores near the surface considerably. After further weathering this portion fractured to a depth of 3-4mm at the surface, rather than along the bedding plane as happened frequently in other Drumbane Rusty samples during weathering. This highlights the problems associated with applying PMCs with excessive nanoparticle content.

Comparisons were also made between cross sections where only one part was subjected to further weathering (Figure 6-20, 5: part on left as treated with PMC, part on right after further weathering, and 4: part on right in (5) during further weathering prior to washing). This shows both the change in appearance likely to occur because of treatment with PMCs and the PMC-treated sandstone after further weathering.

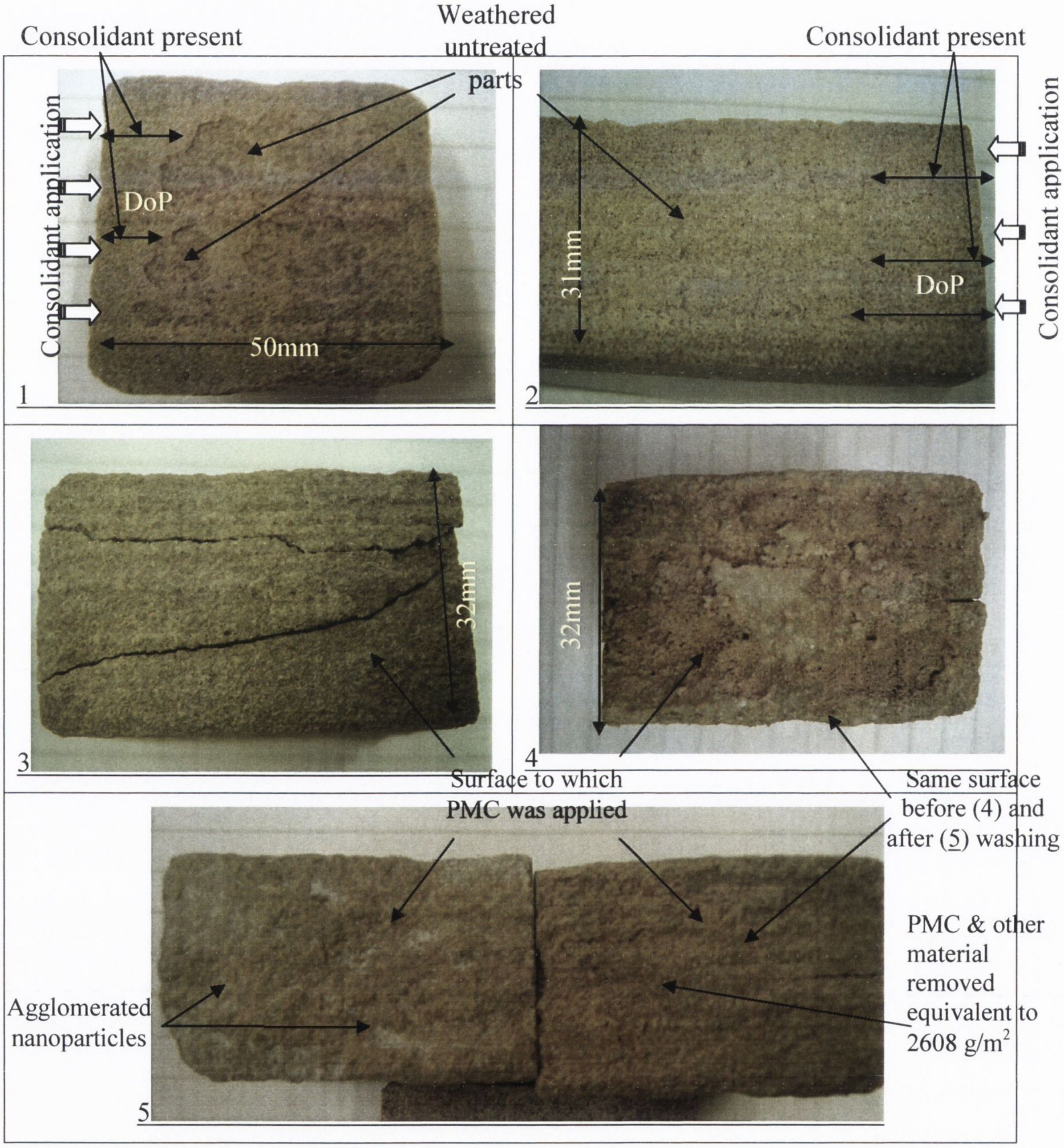


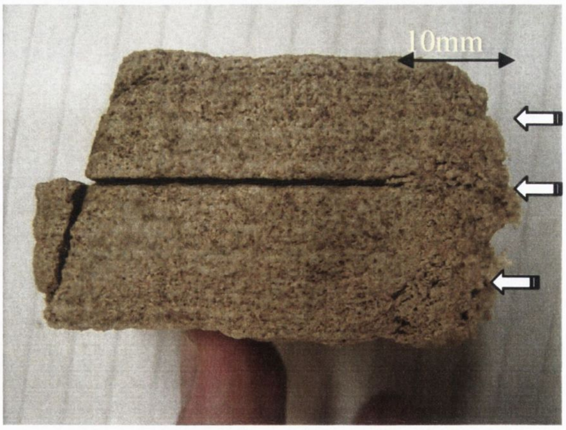
Figure 6.20: Observations on treated sample surfaces after further weathering tests (1-2 cross sections illustrating the depth of penetration, 3-5 halved prisms treated with PMCs showing the material loss caused by pore blockages near surface)

These observations on the depth of penetration of consolidant in the samples allowed verification of the depths of penetration estimated in *Section 6.4.2*, as presented in Table 6-28.

Depth of penetration (mm) Sample	Results of absorption and wetting tests		Observed in cross sections after further weathering	
	Mean	Min Max	Mean	Min Max
Drumbane Grey	12	9	15	4
		15		20
Drumbane Rusty	11	5	11	5
		18		25
Manorhamilton	16	6	12	9
		30		15

Table 6-28: Depth of penetration observed in sample cross sections after further weathering compared with the previously estimated depths of penetration

A further observation was made on the depths to which weathering took hold on untreated samples, as shown in Figure 6-21 below. The material nearest the most weathered surface became very friable to a depth of approximately 10mm, just below the average depth of penetration estimated and observed for that sample (Drumbane Rusty Prisms, 11mm).



Weathering focussed on this surface

Figure 6.21: Effect of further weathering on an untreated sample, showing significant damage to the average depth of penetration of the sandstone type

6.4.4.3 Durability of samples according to treatment type

By comparing the results by treatment type, the effects of the additions of solvent and nanoparticle contents were seen to have affected the durability of the treatments. While the porosity of the groups of samples to which the different treatments were applied were on average quite close and hence quite comparable before treatment, the application of the product and reduction in sample numbers caused some divergence among them, as shown in Table 6-29:

Treatment	No. of cubes	Mass loss per metre square due to further weathering (g/m^2)		Open porosity of samples before further weathering (%)		Open porosity of samples after further weathering (%)	
Wacker	16	160	-15	9.2	2.6	8.2	2.8
			527		17.3		17.9
Wacker +MEK	15	129	21	8.8	3.9	7.3	3.6
			656		15.4		12.3
Wacker PMC	13	475	8	8.2	4.6	10.0	3.1
			2366		15.9		13.3
Tegovakon	11	203	-5	10.6	4.6	7.6	2.8
			1022		16.0		13.0
Tegovakon +MEK	15	230	-17	8.8	4.5	8.1	2.7
			1023		16.7		19.9
Tegovakon PMC	11	278	20	6.6	4.2	9.9	4.9
			881		9.3		12.9
Untreated	20	1679	46	10.0	4.1	9.9	4.6
			4136		18.2		25.1

Table 6-29: Mass loss per unit area and porosity changes in treated and untreated samples due to durability testing according to treatment type (Note: excludes Killaloe samples)

The Tegovakon+MEK treated samples suffered higher losses than the Wacker+MEK ones. This was also true of the Tegovakon treated samples, however the average porosity of the samples to which Tegovakon had been applied was much higher after treatment than that of the samples treated with Wacker. Tegovakon PMC treated samples lost less material than the Wacker PMC ones. The greatest losses due to further weathering were undoubtedly those of the untreated samples, which were between four and thirteen times higher than the others.

Only the samples treated with PMC experienced significant increases in open porosity due to the further weathering, presumably due to the lower porosity that resulted from their application. This demonstrates the extent to which the PMC had blocked some of the pores, following the deposition of agglomerated nanoparticles and gelation of consolidant around the constricted pores. On average the porosity in the other treated samples was reduced. This was presumably due to the presence of salts in the pore system, even after thorough washing.

Chapter 7:

Discussion

Characterisation of Irish sandstone

7 *Discussion: Characterisation of Irish sandstones*

7.1 The influence of the petrographic characteristics on physical properties

The petrographic study of the samples provided both qualitative and quantitative results. The mass structure, moisture transfer and mechanical strength properties determined by laboratory testing echo the findings of the petrographic analysis.

7.1.1 Drumbane sandstone

Wilkinson described Drumbane sandstone as *'grey quartz grain sandstone with argillo-siliceous cement, and slightly micaceous ochrenous spots'*. Its density was determined to be 159.4 lbs/ft^3, which is equivalent to 2553 kg/m^3. It was also calculated that the stone absorbed 2.9 $lbsH_2O/ft^3$ after 88hrs immersion, which is equivalent to 45.6 kgH_2O/m^3 or 1.8% open porosity. The force required to crush a 1" cube of ochreous Drumbane sandstone was 10290 lbs, equivalent to approximately 84 N/mm^2. (Wilkinson 1845)

The stone studied by Wilkinson was slightly different to the Drumbane sandstone used in this study: it was ochreous in colour, not grey or rusty. The studied sandstone contains two distinct compositions depending on secondary porosity characteristics; the Grey and Rusty types vary according to clay mineral and iron oxide content and also on the state of weathering in the stone. The laboratory testing agreed with this, finding that their porosities were 3.7% and 8.0% compared with estimates of 4% and 10% from the thin sections. Their pores were both angular and of low sphericity.

In the Grey samples the pores were fine, however, while those of the Rusty were medium-fine due to the lesser clay matrix content. The latter's capillary absorption was between 27% and 112% higher over the 1st and 2nd 24 hours respectively. Its larger pore sizes also allowed moisture to evaporate between 94% and 172% faster over the same time periods.

The Rusty type contains less quartz and more iron, concentrated in layers and lining the pores created by weathering of the clay matrix. This less homogeneous structure explains the difference in mechanical strength properties. (Grey samples crushed at 42% higher compressive strength: 121 N/mm^2 compared to 70 N/mm^2, and had 23% higher modulus of elasticity: 32 GPa compared to 26 GPa). The more even distribution of matrix throughout the mass of the Grey type provides greater resistance to deformation, whereas the greater variation of contents with depth in the Rusty makes fracture propagation easier.

7.1.2 Manorhamilton sandstone

The Manorhamilton sandstone is fine- to medium-grained pale sandstone. It contains >70% quartz but its porosity is relatively open due to the low clay matrix content. The laboratory testing confirmed it to be 11.0%.

It only has medium capillary absorption despite the high levels of porosity and pore interconnectivity. The pores are subangular to angular in shape because of low matrix content and the quartz grains are platy and sutured. These pore characteristics limit the capillary absorption coefficient found in laboratory testing to 12.7 $g/m^2/s^{0.5}$. It was observed to be 0.6 $g/m^2/s^{0.5}$ during the 2nd 24 hours, the lowest rate of absorption observed in later intervals. The evaporation is medium at a steady rate of between 34 and 37 $g/m^2/hr$, inhibited by the retention of moisture in the tight intergranular pore spaces.

The large deviations in moisture transfer properties are a result of the wide distribution of pore sizes, cement and clay matrix contents. These are observed in the white, buff, yellowish and sandy brown colours, which are ordered from highest siliceous cement content to highest iron content respectively.

These differences are also reflected in the strength characteristics. The packing and sorting of the quartz grains contribute to its medium strength of between 91 and 122 N/mm^2. This is higher than that of other samples of similar and even lower porosity despite the low cement content. Its modulus of elasticity varies between 26 and 45 GPa according to the colour differences, which is a fairly high range compared to the others.

7.1.3 Clara Hill sandstone

The Clara Hill sandstone contains two distinct compositions. The Grey type features high quartz and considerable iron oxide and clay contents with 5-7% porosity. The Yellow type contains less quartz and clay but more iron. It has high porosity, up to 25-

30% in places according to the thin sections. Their open porosities were determined by laboratory testing to be 4.7% and 15.2% respectively.

The pores of the Grey type are fine and subangular but have a wide distribution with a negative skew and as a result have low interconnectivity. The pores of the Yellow type range from coarse to fine and are angular in shape. Their capillary absorption coefficients were determined to be 7.1 $g/m^2/s^{0.5}$ (low) and 19.9 $g/m^2/s^{0.5}$ (high) respectively. Absorption during the 2nd 24 hours is almost equal in the two samples though, at 3.3 $g/m^2/s^{0.5}$. The low pore interconnectivity inhibits earlier absorption in the Grey type. A higher rate of absorption is therefore possible in the long term. The high porosity of the Yellow samples enables similar rates during the 2nd 24 hours. These same attributes affect evaporation, with the Grey's rate decreasing 52% to 12 $g/m^2/hr$ because of the moisture within the inner porosity. The Yellow's rate only decreases 14% to 40 $g/m^2/hr$ because the pores' openness does not inhibit the stone from breathing.

In the Grey type the quartz is well sorted and densely packed with interstitial iron and clay cements. Its low strength characteristics must therefore be due to the lack of siliceous cements. The low strength of the Yellow type is due more to the variation of content, especially the widespread clay minerals, and less dense packing of the constituent grains and matrix. Their compressive strengths were estimated to be in the range of 48 N/mm^2 to 76 N/mm^2, with the Yellow's much towards the lower end of the range. The modulus of elasticity of the Clara Hill samples was measured to be in the range 10 GPa to 18 GPa, with the Yellow's again closer to the lower end of the scale.

7.1.4 Killaloe sandstone

The appearance of Killaloe sandstone is very variable although its composition is quite similar. The colour varies between Buff, Grey-Green, Ochre and Dark Grey, of which only the first two were studied in thin sections.

The stone is generally very dense and well packed with fine to very fine pores. The Buff type contains abundant medium to fine quartz, along with iron oxides and clay minerals, bonded with siliceous cements. The Grey-Green type contains medium quartz and is poorly to moderately well sorted. The Ochreous type displays similar characteristics to the Buff type and is perhaps the result of greater oxidation. The Dark Grey contains intrusions of very dense light grey material surrounded by medium-coarse dark grey material, most of which is quartzitic. Lab testing determined their average open porosities to be 2.3%, 1.5%, 2.7% and 8.3% respectively. These contradict those observed in the thin sections slightly (Buff 1%, Grey-Green 2-5%), however they are still low. This suggests that the porosity of the Grey-Green may vary more so than the others.

Their low porosity is responsible for their low capillary absorption. The Buff and Grey-Green also have low evaporation for the same reason, while the Ochre and Dark Grey have medium and high rates respectively. This is because of fracturing in the former and medium porosity in the latter.

The low porosity and cement content of the Buff influence its high strength (140-221 N/mm^2, 23-63 GPa). The abundant siliceous and occasional dolomite cements of the Grey-Green provide medium-high strength characteristics, because of its variable cement contents and low porosity (89-125 N/mm^2, 23-41 GPa). Its surface hardness is also high, as is that of the ochre and dark grey samples. The strength of the other two sample types should be lower because of occasional fractures and high porosity regions respectively.

7.2 Relative classification of properties

Relative classification of the properties for the samples will help later discussions, as defined in Table 7-1 and used in Table 7-2.

Property	Classification			Units
	Low	Medium	High	
Apparent density	<2300	2300 – 2500	>2500	kg/m^3
Open porosity	<5	5 – 10	>10	%
Capillary absorption	<6	6 – 15	>15	$g/m^2/s^{0.5}$
Evaporation	<25	25 – 40	>40	$g/m^2/hr$
Compressive strength	<80	80 – 110	>110	N/mm^2
Modulus of elasticity	<20	20 - 40	>40	GPa

Table 7-1: Ranges of values for classification of samples – low, medium and high

Sample	Apparent density	Open porosity	Capillary absorption	Evaporation	Compressive strength	Modulus of elasticity
Drumbane Grey	High	Low	Low-Medium	Medium-High	High	Medium-High
Drumbane Rusty	Low-Medium	Medium	Medium-High	High	Low	Low-Medium
Manorhamilton	Medium	High	Medium-High	Medium-High	Medium	Medium-High
Clara Hill Grey	Medium	Low	Low-Medium	Low-Medium	Low	Low
Clara Hill Yellow	Low	High	Medium-High	Medium-High	Low	Low
Killaloe Buff	High	Low	Low	Low-Medium	High	Medium-High
Killaloe Grey-Green	High	Low	Low	Low	High	Medium
Killaloe Ochre	High	Low	Low-Medium	Medium	-	-
Killaloe Dark Grey	Low-High	Low-High	Low-High	Low-High	-	-

Table 7-2: Classification of samples by properties in low, medium and high ranges

There is a wide range of variation in the measured properties. The range of values chosen for Low, Medium and High are evenly distributed and the numbers assigned to each are relatively similar. These values agree with those obtained by previous authors.

For example, sandstone density varies between 2000 kg/m^3 and 2600 kg/m^3, while porosity ranges from 5% to 25% (Winkler 1975). The minimum quality sandstone allowable according to *'ASTM C616 - Standard Specification for Quartz Based Dimension Stone'* has density of no less than 2160 kg/m^3 and porosity of no more than 20%. For quartzitic sandstone (greater than 90% quartz) these values should be 2560 kg/m^3 and 3% respectively. The lowest density sample, Clara Hill Yellow has a density of almost 2200 kg/m^3 and porosity of up to 25%. The highest density sample, Killaloe Grey-Green has a density of well over 2600 kg/m^3 and porosity of 2%.

Chapter 8:

Discussion

Durability and weathering of Irish sandstone whether treated or not

8 Discussion: Durability and weathering of Irish sandstones whether treated or not

8.1 Effects of salt crystallisation cycling on samples

The salt crystallisation method followed a method similar to the RILEM recommendations and BS EN standards in order to recreate the decay at the monuments. Partial immersion of the samples was used in order to promote greater corrosion on the exposed surfaces.

Hence the decay forms achieved by laboratory testing were representative of the decay observed in the monuments. The salt crystallisation breaks the cohesion between the cements, grains and matrix minerals, mimicking the effects of dissolution processes in causing granular disintegration, differential erosion and flaking, as discussed in *Section 3.1.4*.

Fracturing was also observed in some samples. The mechanism of fracturing occurs more frequently during artificial weathering than would occur by gradual weathering in atmospheric conditions. The crystallisation pressures in the pores are higher than any caused in normal monumental conditions, as discussed in *Section 3.1.5*, and are hence more likely to exceed the stone's strength.

The severity and extent of the decay varied according to each of the samples' individual composition and properties, as discussed in the following pages.

8.1.1 Drumbane sandstone

The flaking observed in the Grey samples was due to the removal of clay matrix from near the surface. This increased the surface area and lead to 8-15% higher evaporation. This was evident on the top face of the cubes (where clay content was higher) (Figure 8-1,1). Fracturing occurred because of salt crystallisation in fine pores and propagated along planar weaknesses (3). The average mass lost was 215 g/m^2, and porosity increased to 4.1%.

Differential erosion affected the structure of the Rusty samples, removing layers of lower clay matrix content and higher iron oxide content. This increased the surface area, resulting in higher evaporation rates. Fracturing was also observed to occur during rehydration of the salt crystals, presumably exceeding the strength of the stone within the fine pores. The fractures propagated through the stone quite easily due to the layered structure, resulting in higher capillary absorption (2 and 4). Average mass losses were 504 g/m^2 for the Cubes and $1316/m^2$ for the Prisms. Their porosity increased to 8.6 % and 13.0 % respectively.

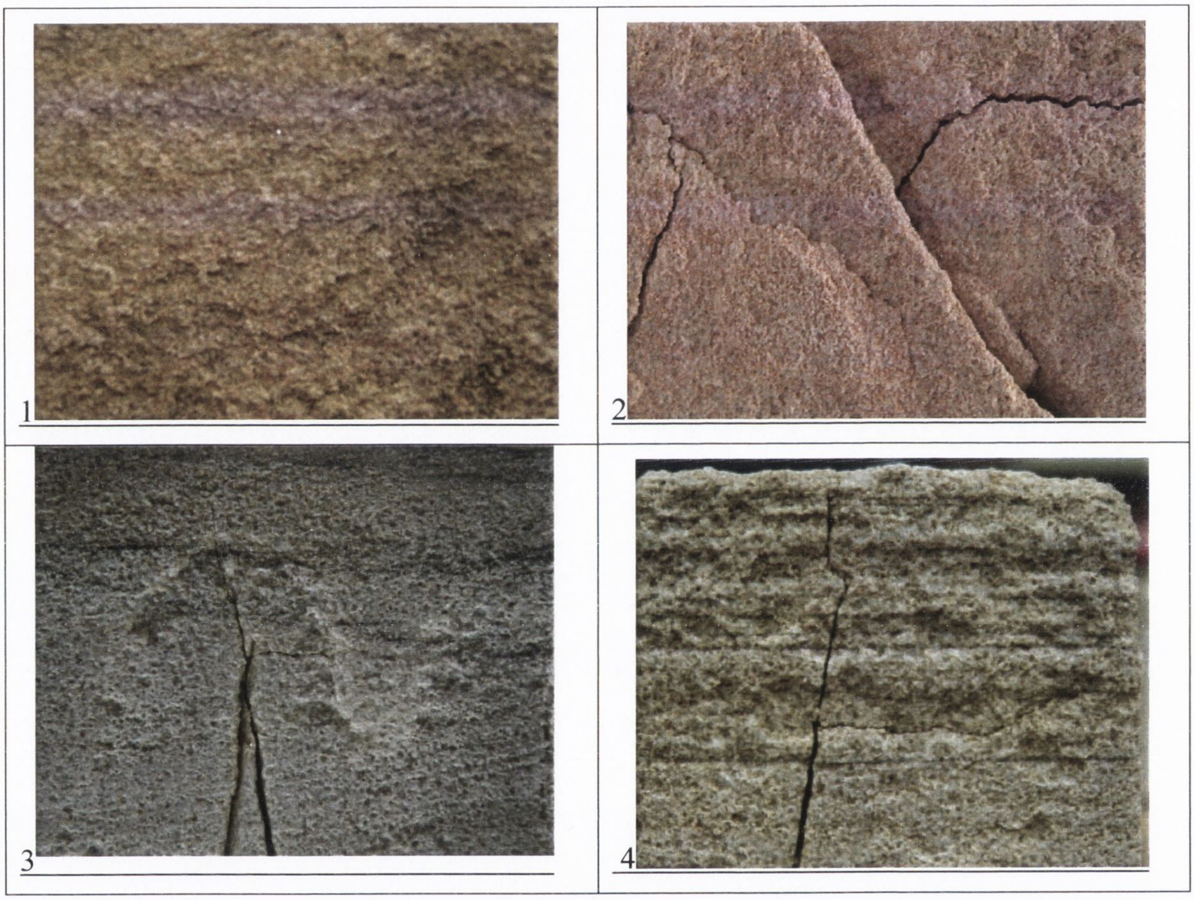


Figure 8-1: Decay effects observed in Drumbane sandstone samples due to artificial weathering -Grey (left, 1-looking onto bedding and 3-along) and Rusty (right, 2-onto bedding and 4-along)

8.1.2 Manorhamilton sandstone

The weathering of the ferruginous cements caused mineral discolouration to various extents (Figure 8-2). Flaking occurred because of long term evaporation rates and salt crystallisation just below the surface during cycles (2 and 4). Granular disintegration also occurred on the exposed surfaces as there was little clay matrix content to protect the sparse interstitial siliceous cements. Their strength was overcome by the salt crystallisation pressures. Differential erosion was evident in some samples, due to irregular layers of low cement content (1, 2 and 3). These irregularities lead to lower capillary absorption and higher evaporation rates. The average mass loss was relatively high at 779 g/m^2, and average open porosity increased to 11.6%.

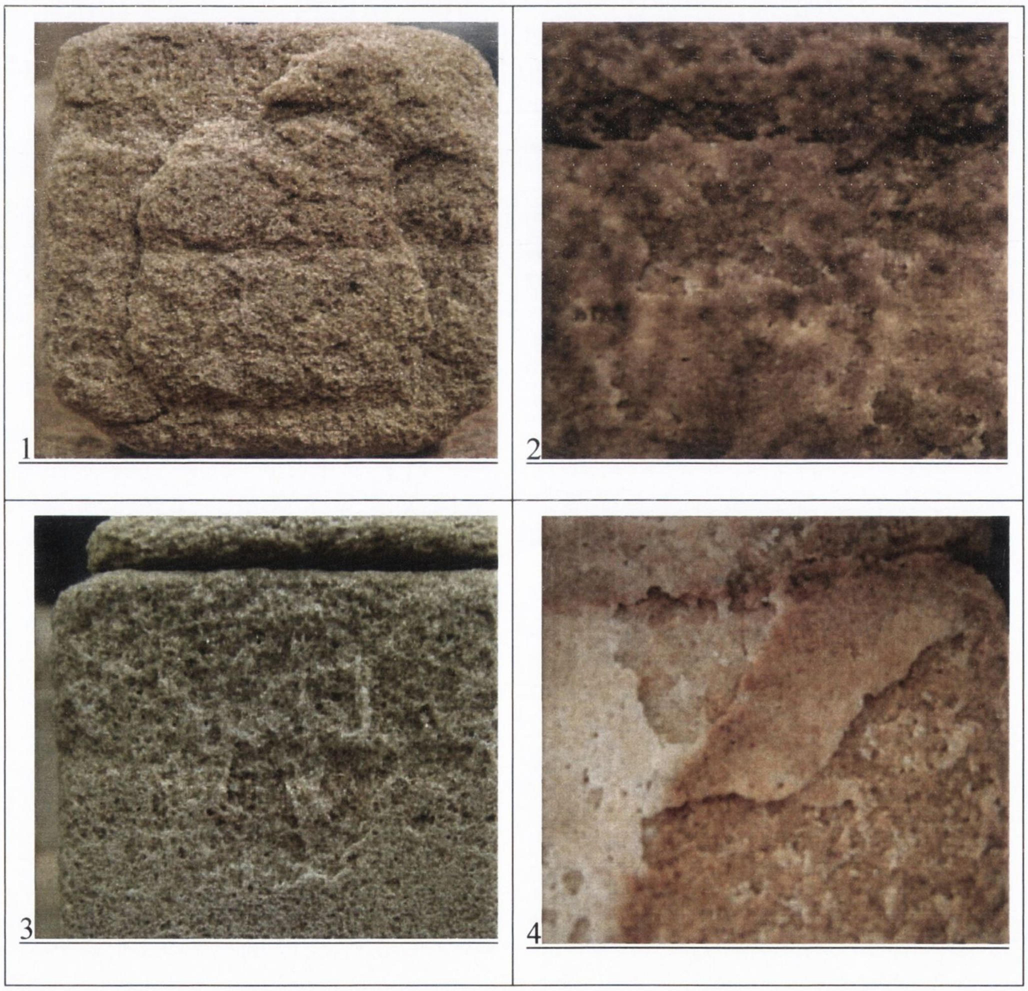


Figure 8-2: Decay effects observed in Manorhamilton sandstone samples due to artificial weathering (all looking along bedding)

8.1.3 Clara Hill sandstone

Salt crystallisation in the fine pores caused fracturing in the Grey sample, and its low strength was easily overcome (Figure 8-3, 1). Flaking occurred where siliceous content was higher. The removal of ferruginous cements caused granular disintegration and mineral discolouration (3). Average mass loss was 643 g/m^2. Porosity was increased to 6.4 %. Some fractures caused greater loss of material. This was most likely due to salt crystallisation in poorly interconnected fine pores.

Differential erosion occurred in the Yellow samples because of its high porosity and concentrated clay contents. The poor strength of the cements also resulted in granular disintegration so the constituent grains were easily dislodged. 1973 g/m^2 of material was lost on average and the average open porosity increased from 15.2 % to 16.4%. Capillary absorption and evaporation were greatly increased in both samples, however long term evaporation was reduced in the Yellow.

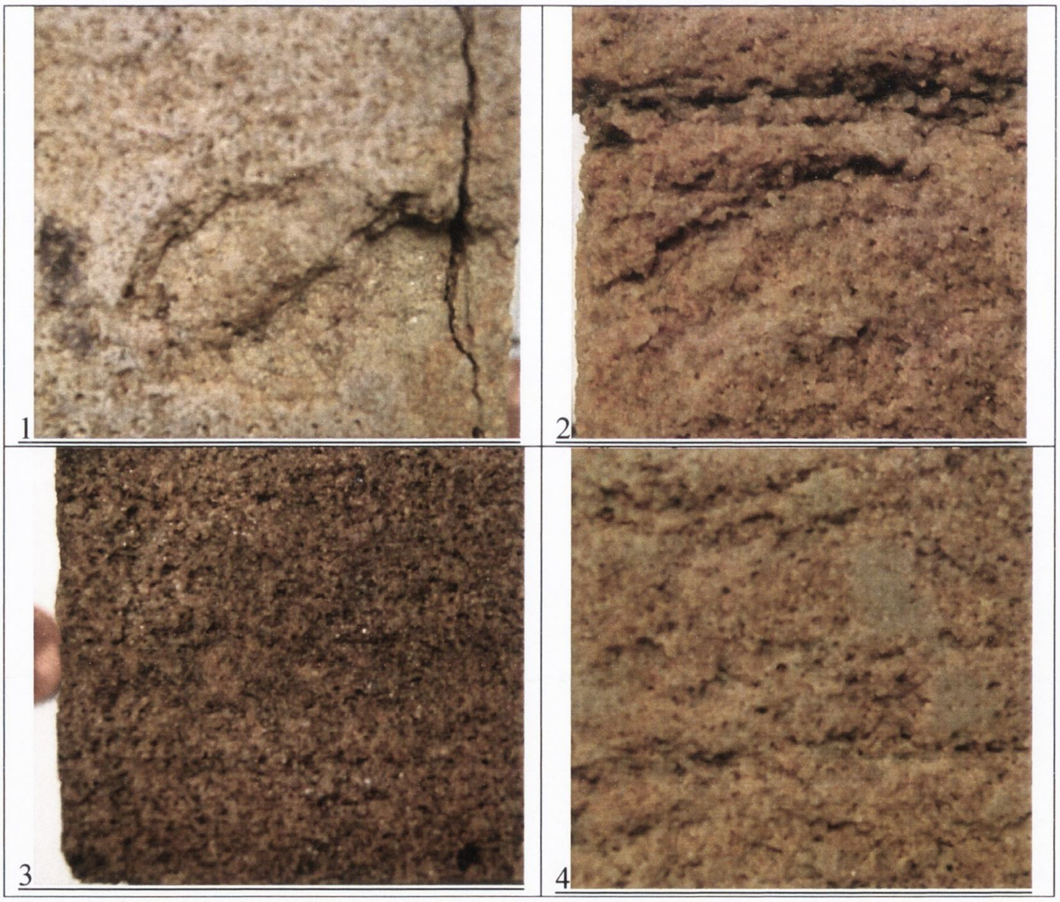


Figure 8-3: Decay effects observed in Clara Hill sandstone samples due to artificial weathering -Grey (left, 1 and 3-both looking onto bedding) and Yellow (right, 2 and 4-both along bedding)

8.1.4 Killaloe sandstone

Very small amounts of weaker, more porous material were lost from the surfaces of the Killaloe samples. Open porosity decreased to even lower values as the removal of the salts by washing was more difficult in the low porosity samples (by -0.1%, -0.3%, -0.3%, -0.7% (1)-(4) in Figure 8-4 respectively). Capillary absorption was also reduced by the presence of salts. Evaporation increased in all but the Dark Grey samples however.

Slight discolouration was caused by weathering of the iron and was most evident in the buff sample (1). Differential erosion removed material from the ochre sample where discontinuities were present (3). Much material was removed from the high porosity parts of the dark grey sample, causing granular disintegration and differential erosion (4). This was probably due to weaker cementing of the constituent minerals.

Figure 8-4: Decay effects observed in Killaloe sandstone samples due to artificial weathering -Buff (1), Grey-Green (2), Ochre (3) and Dark Grey (4), all along bedding

8.2 Assessment and classification of mass losses per unit area

The main indicator of the decay caused is the mass loss from the samples. In order to give comparative values for other studies to relate these weathering results to those obtained either in other lab tests or in studies of monuments, the appropriate area over which the weathering occurred was required, as presented in *Section 6.2.3.2*.

It should be highlighted that this is considering the planar area of the cube faces, not the specific surface area of the sandstones. Both are relevant measures and serve different levels of information in the field of stone conservation. The former is easily surveyed for exposed monumental surfaces, and can be calculated for both monuments and samples. The latter is a useful sample property, and may offer certain advantages to research and further studies. It provides an accurate measure of porosity characteristics but it is also rarely measurable on monuments and is more susceptible to sample variability. For these reasons it was not determined.

While the relevant standards and recommendations (EN 12370:1999 and RILEM PEM-25), avoid the need for such comparative calculations by controlling cube dimensions and deviations, the results are still presented as being a volumetric mass percentage, which is imprecise due to both structure and arrangement. Samples may not always be available or suitable within the prescribed limits. The loss of material requires that mass move away from the surface of the sample. Hence it is most representative to assess the apparent flux of material caused by weathering.

The effective planar surface from which material was lost was calculated by estimating the extent of weathering on each cube face using the dimensions and photographs taken. The severity of the losses was not assessed, as the calculated loss of material accounted for this directly. It should be mentioned, however, that the face at the bottom during salt immersion was generally substantially less affected, and so was often omitted.

Turkington and Smith (2000) noted that the distribution of salts within stone is not accurately determined by estimation of their presence in studies of a single surface (*Section 3.1.5.5*). The consideration proposed here does not conflict with this. If anything, in fact, it assumes a similar attitude to the assessment of material losses from surfaces.

Ranges can easily be devised to classify the percentage loss as low, medium or high, as shown in Table 8-1:

Weathering classification	Percentage loss (%)			Loss per unit area (g/m^2)	
	Range	Sample mean			Range
Low	0.0 – 1.5	0.1	Killaloe Buff	35	0-250
		0.3	Killaloe Ochre	70	
		0.3	Killaloe Grey-Green	77	
		0.8	Drumbane Grey	215	
Medium	1.5 – 4.0	1.7	Killaloe Dark Grey	396	250-1000
		2.2	Drumbane Rusty (Cubes)	504	
		2.9	Clara Hill Grey	643	
		3.5	Manorhamilton	779	
High	> 4.0	5.6	Drumbane Rusty (Prisms)	1316	> 1000
		8.5	Clara Hill Yellow	1973	

Table 8-1: Ranges for the classification of sample weathering according to percentage mass loss and mass loss per unit area

It can be seen in this table that comparisons between the percentage mass and the mass lost per unit area in many of the samples do not show any big differences. The range of values is much lower when percentage masses are considered. The errors associated with the larger values of mass per unit area are of the same order, but the results are more insightful for other practitioners.

Irrespective of which results are considered, the Killaloe samples were shown to have weathered the least and the Clara Hill samples to have weathered the most. The mass losses in the Drumbane samples varied due to differences in shape, composition and porosity. In highlighting the two samples in the High classification it can be pointed out that both contained high iron content, high clay matrix content and medium-high porosity. The Manorhamilton samples were more durable than these two, presumably due to the dense packing of the quartz grains and the strength of the siliceous cements.

8.3 Variation of properties according to decay type

The changes brought about in the samples' mass structure and moisture transfer properties by artificial weathering were averaged according to the decay types observed. The results were not conclusive as the standard deviations were too high as shown in Table 8-2. Some indicative qualities were noticed however:

- Granular disintegration and differential erosion result in higher mass losses
- Porosity, capillary absorption and evaporation are more likely to increase as a result of weathering
- Differential erosion is less likely to increase porosity
- Evaporation is increased most where flaking occurs
- Fracturing involves greater increases in capillary absorption

Decay type	% change in:			
	Mass	Porosity	Capillary	Evaporation
Granular disintegration	-4.2±2.7	+16±24	+22±50	+55±49
Flaking	-2.4±1.4	+17±16	+15±20	+110±42
Differential erosion	-4.1±3.8	+3±22	+10±45	+32±33
Fracturing	-3.1±2.3	+29±15	+43±25	+83±59

Table 8-2: Average and standard deviation of percentage changes in mass structure and moisture transfer properties according to decay type

Differential erosion is less likely to increase porosity by a large amount as the higher porosity material is removed. The differences between the flaking and granular disintegration may be attributed to the strength and extent of cohesive constituents. The grains in a flaked stone are more strongly cemented. Greater absorption is possible in fractured stone because extra pores have been opened up. Greater evaporation is possible in flaked stone because moisture is spread along thinner parts at the surface.

8.4 Comparison of weathering observed in laboratory testing and during fieldwork

8.4.1 Drumbane sandstone and Cormac's Chapel

The differential erosion and granular disintegration in the west doorway and façade were successfully recreated in the laboratory, as shown in *Sections 4.2*, *6.2* and *8.1*. The clay matrix content was eroded, exposing the ferruginous cements and reducing cohesion between constituents. The exposure of the west façade would have left the stone susceptible to granular disintegration due to the impact of wind-borne dust, for example.

The flaking observed in the east doorway was simulated to a small but not as severe extent in some of the samples. Based on the difference in composition between the Grey and Rusty samples, it may be assumed that there is higher clay matrix content present in the stone on the east façade because of the sheltered location. Increased evaporation was also measured in the samples, as described in *Section 6.2.1.2* and discussed later on in *Section 10.1.1*. Long term high moisture content has caused the loss of cohesion just below the surface of the stone.

8.4.2 Killaloe sandstone and St. Brendan's Cathedral

The variability in colour in the doorway of St. Brendan's Cathedral was seen in both the unweathered and weathered samples of Killaloe sandstone. As shown in *Sections 4.2*, *6.2* and *8.1*, the Killaloe Dark Grey samples are more representative of the sandstone in the monument: mass losses calculated per unit area in Killaloe Dark Grey samples ≈ 400 g/m^2.

Killaloe sandstone is very durable so granular disintegration was only seen to a slight extent in the samples. It contains densely packed quartz grains and not much clay matrix. It is secondary silicate content that is predominantly present between the grains.

The proximity of the cathedral to groundwater and the past use of impermeable paving at the doorway have caused continuing high moisture conditions in the stone. The lengthy exposure of the monument to the combined effects of moisture transfer, silica dissolution and salt crystallisation has resulted in granular disintegration.

An estimation of the progress of the dissolution of siliceous cements within the sandstone at the doorway may be based on the values reported from Strakhov in *Section 3.1.4.1* using the diffusion rate model of Hoke & Turcotte mentioned in *Section 3.1.4.2*. According to the former, an appreciable 20% reduction in silica content from 85% could occur in as little as 700 years or as much as 1400 years. Given the anecdotal evidence of Leask (*Section 1.1.2*), the incubation period may be adjudged to have ended in the later half of the 20th century, about 800 years after construction.

There are three key parameters involved in this process: mass, time and moisture. The rate of dissolution would now be reliant on the sustained presence of appreciable moisture content to maintain the dissolution of the silica cements since then. It must be assumed that this is proportional to capillary absorption (because of moisture's influence and the square root of time relationship), and that dissolution is only effective on the proportion of cements in the sandstone.

Once salt concentrations are present, the distribution of moisture within stone is affected. They combine during crystallisation, and thereby provide resistance to evaporation. Stresses develop in the pores, as described in *Section 3.1.5*. The rate of silica dissolution is then negligible in comparison.

8.5 Effects of weathering and treatment on mechanical strength

The changes in compressive strength and modulus of elasticity presented in *Section 6.4.1.3* suggest that the decay processes and consolidant treatments affect the cohesive action between the grains, cements and fine matrix in sandstone. The lack of suitable samples reduced the reliability of the data however.

It was observed that decay affected the samples to varying degrees, depending on whether significant material losses occurred or not. On average both the compressive strength and modulus of elasticity was reduced by between 15% and 50%. Exceptional results were obtained on several samples; both the compressive strength and modulus of the weathered Killaloe Grey-Green samples were approximately 30% higher.

Treatment was observed to have increased the modulus of elasticity of most samples, the only exception being the Killaloe Buff ones. Improvements were in the range of 20% to 30% on average. In the treated Manorhamilton samples, the increases in modulus were accompanied by reductions of up to 70% in compressive strength, resulting in brittle failure. Reasons for this include weathering effects and the nature of consolidant treatment;

- alteration of iron oxide cements in pores (mineral dissociation observed), compromising the bonding capacity of the cements and weakening resistance to deformation
- lower fine matrix present between grains to provide resistance to strain
- differential capacity to withstand strain between outer treated areas and the mass of weathered sandstone below, and thereby inducing possible planes of weakness if stress distribution is insufficient.

It is suggested that treatment of sandstone with TEOS consolidants can in most cases increase mechanical strength. There are several factors that are likely to reduce their effectiveness, mainly associated with the cementing and cohesive actions of constituents, and the effects of weathering on these.

8.6 Durability of consolidated Irish sandstone to further artificial weathering by comparison of weathered and treated samples

The durability of the treated and weathered sandstones was compared by using the artificial weathering method on the samples again. Judging by the samples' visual appearances it seemed that the second weathering caused more decay to all samples than the first, regardless of the consolidant treatment.

The material changes that occurred in the samples due to each of the weathering and treatment processes are compared in Table 8-3 on the next page, in more detail than Table 6-29 in *Section 6.4.4.3*. Any relationship between the losses due to weathering and the gains due to treatment are not so obvious. There is a difference between the calculations of these, as the losses of material from the cubes occurred on several faces, but the application of treatments was through only one. Comparisons in the losses due to weathering do offer several indicators as to the effectiveness of consolidant treatments however.

The magnitude of losses during the 2nd series of crystallisation cycles was more often less than the magnitude of those of the 1st. This is compelling evidence that TEOS treatments provide the desired consolidating effect and that they reduce the rate of weathering.

Sample	No.	Weathering		No.	Treatment		No.	Weathering(2nd)		No.	Weathering(2nd)		Ratio
	U∩W	Loss (g/m^2)		W∩T	Gain (g/m^2)		T	Loss (g/m^2)		W	Loss (g/m^2)		W/T
Drumbane Grey	26	215	73 586	20	375	174 752	19	112	-105 689	3	539	232 787	4.8
Drumbane Rusty (Cubes)	12	504	311 763	10	468	152 1008	4	295	61 850	1	1583	- -	5.4
Drumbane Rusty (Prisms)	14	1316	705 2330	11	1020	441 1510	10	1430	483 3608	3	9500	8458 10175	6.6
Manorhamilton	38	779	156 3086	30	1112	515 3925	26	139	0 268	6	665	332 1030	4.8
Clara Hill Grey	22	643	108 4226	19	815	282 2223	9	530	110 1370	4	2861	1875 3489	5.4
Clara Hill Yellow	16	1973	196 5039	12	1322	501 2473	9	779	195 1580	3	2985	2508 3333	3.8
Killaloe Buff	13	35	0 60	12	117	42 197	8	-62	-81 -43	2	-39	-91 14	0.6
Killaloe Grey/Green	14	77	26 225	11	131	60 256	8	-11	-14 -8	2	0	-3 2	0
Killaloe Ochre	5	70	51 85	4	194	150 267	3	90	38 150	1	-13	- -	-0.1
Killaloe Dark Grey	6	396	50 669	6	577	175 742	3	283	225 321	0	-	- -	-

Table 8-3: Comparison of changes in mass per unit surface area due to weathering (W) and treatment (T) of sandstone samples concentrated on one surface. The number of cubes of each lithotype is shown (mean, minimum and maximum values). Note that a negative value indicates salt accumulation.

With the proportions of decay indicating that consolidant treatment is favourable, the effectiveness of each treatment merits greater attention to see what effects the mass structure and other sample specific characteristics have on treatment success.

The Drumbane Rusty and Clara Hill samples lost greater quantities of material due to the 2nd series of weathering than either the Drumbane Grey or Manorhamilton ones did. Only the Killaloe samples lost little or no mass whether treated or not. In fact it was the treated Killaloe samples that tended to either lose most material or gain lower quantities of salt. These samples had already been proven to be very durable however, so their behaviour during weathering in this condition is of lesser significance. On the other hand, several of the Clara Hill Grey cubes lost significantly more because of fracturing and crumbling to depths in the range of 5-10mm and it was clear that treatment was not sufficient to prevent them weathering to the point of failure.

Of the other samples, those that were weathered (and left untreated) suffered manifold the material losses of the treated samples when subjected to further weathering. The lowest ratio of material lost between the treated and weathered samples during further weathering was that of the Clara Hill Yellow sandstone. On average weathered Clara Hill Yellow samples lost approximately 3.8 times more material than treated ones.

It is believed that this was due to the openness of the pores and size of constituent grains. As mentioned in *Section 3.2.2* there is an upper limit to the size of particles that TEOS can consolidate. From this it is suggested that TEOS consolidants are less potent in improving resistance to weathering significantly where porosity is high and a lack of matrix materials is present to protect the cements and aid consolidant bonding. To deal with this, appropriate PMC treatments may increase the levels of bonding that occur in sandstone lacking matrix materials. This does not hold true when the Drumbane Grey and Manorhamilton samples are compared however, both of which have the next lowest ratio of 3.8. Hence the ratio between weathered/untreated and treated rates is considered to be an indicative measure that is independent of decay types and individual sample characteristics.

For the most part, treatment of sandstone with consolidants resulted in material losses during a 2nd series of cycles that were lower than those caused during the 1st. At the same time the losses caused in those that weren't treated generally increased when further weathering occurred.

Apart from the scale of losses, the most obvious disparity observed during further weathering was in the PMC treated samples where blockages in the pores inhibited salt penetration. Crystallisation was concentrated nearer to the surface because of this and, on one occasion, the associated higher modulus lead to fracturing of the treated area up to a depth of approximately 5mm.

It is encouraging that this only happened once out of all of the samples. Based on the changes in porosity shown in Table 6-29 the samples to which the PMCs were applied were greatly affected by the further weathering. As a group they were vulnerable to this fracturing, yet it was in just one cube out of at least twenty that was actually affected. Furthermore the levels of blocking ought to be much lower if nanoparticle contents are reduced, as discussed in the following chapters.

Chapter 9:

Discussion

Addition of solvents and nanoparticles to consolidants and their effects on application and performance

9 Discussion: Addition of solvents and nanoparticles to consolidants and their effects on application and performance

9.1 Modification of consolidants with solvents and nanoparticles

9.1.1 Differences in gelation processes of consolidant products

The progress of evaporation of the condensation products from the gels was different for the two commercial consolidants, as shown in Figures 6-10 and 6-11. This was because of the variation in the degree of polymerisation and the catalyst concentrations of the Wacker and Tegovakon treatments. The solvent and particle contents did not influence this much despite altering the percentage composition.

The differences in the evolution of bonding had slight effects on the resulting silica film, whether formed in a sandstone pore system or in a Petri dish. The shapes described in *Section 6.3.1, Characteristics of consolidant gels* were all formed by differential stresses caused by:

- evaporation of the condensation by-product, ethanol, or
- compliance of the gel in shrinkage movements.

The Wacker OH-based gels condensed and gelled faster, in agreement with previously reported gelation times (Brus and Kotlik 1996). This explains why the Tegovakon gels were less cracked in the early stages of condensation. The gels demonstrated the timing and balance between shrinkage and compliance, and how the stresses developed.

9.1.2 Addition of solvents for deeper penetration and reduced gel thickness

As mentioned in *Section 3.2.3.4*, solvents have often been added to consolidants to aid penetration or reduce the thickness of the film deposited in the stone. The depth of penetration may be increased and the likelihood of blocking fine pores is reduced. This is most relevant where porosity or the interconnectivity of the pores in the sandstone is low. The addition of solvents also increases the amount of evaporation from the sample that must occur during gelation and the amount of mass deposited may also be affected. The average mass of consolidant deposited was either slightly reduced or as good as that in the others, as shown in *Section 6.3.2*. This was due to a combination of the consolidants' liquid properties and the samples' porosity.

The TEOS+MEK products emulated the previous incarnations of commercial consolidants containing approximately 20-25% ketone solvents. This provided relevant information on the difference between diluted and non-diluted TEOS. Only the MEK solvent was tested in consolidant application to sandstone samples however. The quality of the results may have been compromised if both MEK and Isopropanol had been used as the number of cube samples would have been too low to accommodate each of the permuted combinations. Isopropanol seemed to form much smoother gels due to its lower surface tension and vapour pressure. It does have higher viscosity however, thereby defeating the purpose.

9.1.3 Addition of nanoparticles: effects on viscosity, aggregation and bonding

The previous studies of PMC's (see *Sections 3.2.3.5-6*) principally used 10-20nm diameter particles of silica in isopropanol to provide steric stability to the larger oxide nanoparticles: e.g. 200nm titania and 300nm alumina. Between 5% and 10% by volume of particulate content remained dispersed as sols and were stable for several days. These were prepared by successive addition of solvent (up to 50%) and of oxide nanoparticles during mixing and ultrasonic pulsing in an ice-bath for 15 minutes, until the particulate dispersion was at the correct content. Viscosity was seen to increase greatly if the ratio of larger particle to smaller particle content was greater than 9:1. The viscosities were 2.4 mPa.s and 2.8 mPa.s, for their SiO_2-PMC and Al_2O_3-PMC respectively.

Rather than copy the aforementioned PMC compositions the PMC treatments for this study were chosen to contain (by volume):

- 65% TEOS product – high to ensure bonding capabilities of sol-gel remain high
- 11% MEK – low solvent content to achieve a high proportion of deposited material
- 20% 10nm silica
- 5% 45nm alumina – small particle sizes to encourage attractions

The PMC would undoubtedly have strong consolidating ability. The low solvent content would show what effect poor penetration (one of the greater risks discussed in *Section 3.2.4*) might have. Poor preparation techniques were also chosen to demonstrate what would happen if there were problems in mixing PMC's on site.

The rate constants for the aggregation of the particle sizes are shown in Table 9-1 (after Gregory, in Fendler & Dékány, 2004):

Aggregation type	Particles' diameter (nm)		
	Both 10	Both 45	One 10, One 45
Perikinetic	5.0±0.5 e-18	5.0±0.5 e-18	8.3±1.1 e-18
Orthokinetic	4.0±1.9 e-22	3.7±1.7 e-20	8.3±3.9 e-21
Differential settlement	-	-	2.7±0.4 e-26

Table 9-1: Rate constants for perikinetic, orthokinetic and differential settlement aggregation of 10nm and 45nm diameter nanoparticles

The majority of aggregation occurred due to mutual attraction (perikinetic) and less so because of collisions during mixing (orthokinetic and differential settlement).

As outlined in *Section 6.3.2* the increases in the viscosity of the applied PMC gels were quite small, up from approximately 1-1.2 mPa.s to 2-2.4 mPa.s for solutions containing 11% solvent and 25% volume of particles (Figure 6-13). These would have been somewhat higher if the particles had been dispersed in an ultrasonic bath however.

The thickness and deformations observed in the PMC gel plates, as presented in *Section 6.3.1* and Figure 6-11, demonstrate the greater capabilities of PMC's in increasing sandstone's modulus of elasticity. The ability of the particles to aggregate and accumulate interstitially may also serve to increase the distance between constituent grains that TEOS consolidants may bond.

9.2 Application of modified and unmodified consolidant treatments

A standard approach to application is required for treatment to be successful. A strategy to accommodate for the variation of the stone's composition and condition should be identified. Modifications should be made according to the stone's porosity characteristics and the type of weathering observed. Where porosity is lower solvents may be suitable. Where it is higher low particle content PMC's may be suitable.

The type of weathering present may influence the area that is most easily protected. Where flaking or granular disintegration is present and the gaps to be bonded are too large at the surface, consolidation can only be expected to provide weathering resistance to the substrate below. Some of the outermost material may have to be sacrificed, especially if friable material must be touched during application. It is highly unlikely to last much longer without treatment. However if the grains are of a suitable size then it may be suitable for preconsolidation, as discussed in *Section 3.2.3.1*. PMC's may be more suitable in this respect, although this should be determined using a field trial.

It is best to concentrate on one stone element at a time, progressively applying consolidant to its entire outer surface. This should be repeated as appropriate until no more is absorbed. In some cases it may be preferable to remove the pointing mortar either below or around the stone so that the consolidant may penetrate deeper into the stone. This could also allow for greater retention of runoff consolidant, thereby protecting the surfaces below. Repointed mortar would perform better as consolidation would not have reduced its moisture transfer.

For best results the manufacturer's instructions (as mentioned in *Sections 3.2.3.2* and *3.2.3.3*) should be thoroughly analysed and all conditions prepared accordingly:

- Personal protective equipment (PPE) is required by all persons working nearby; breathing apparatus, safety goggles and gloves.
- Appropriate relative humidity and surface temperatures should be ensured to facilitate condensation.
- Protection against sunlight and wind should be provided to prevent excessive evaporation.

Wetting the surface with solvents beforehand may enable deeper penetration of the consolidant. Liquids are primarily encouraged to spread over the application surface to minimise pressures. They are absorbed along surfaces at and near atmospheric pressure in advance of absorption into the stone by capillary pressure. To avoid this, an appropriate solvent should be applied to the surface just before application.

Brushing gives more control than some of the other options. As much of the product should be applied as possible, giving the surface a good 'wipe' or 'squeeze' with a solvent-soaked sponge afterwards to remove excess.

Evaporation of the solvent may occur so the concentration of the applied solution may vary slightly. The solvent evaporates preferentially so the proportions of nanoparticle additions may be greatly increased towards the latter stages of application when PMC's are used. At this time the nanoparticles are more likely to be aggregated so the accumulation of flocs at the surface is most probable if it they are applied. This should be avoided, and fresher solution applied instead.

The progress of the gelation should also be monitored. The outlook for the weather conditions should be considered for the weeks both preceding and following application. The expected progress of the rate of evaporation of any solvent contents and reaction products should be considered. The degree of polymerisation and catalyst content of treatments can be compared using samples spread in a Petri dish and left in similar conditions to the monument. For quicker gelation times, high percentage TEOS products such as Wacker are better. If longer gelation is preferred, lower percentage TEOS products such as Tegovakon are better.

9.3 Performance of modified and unmodified consolidant treatments

The following sections consider the performance of consolidant treatments based on factors other than the durability of treated samples to further weathering, as in *Chapter 8*.

9.3.1 Depth of penetration and absorption

As mentioned in *Section 6.4.2* the presence of consolidant treatment was observed to be slightly darker in some samples. The depths of penetration determined, as shown in Tables 6-22 to 6-26, were quite modest (average 12mm, range 5mm to 30mm) in comparison with the recommended range of 20-25mm (see *Section 3.2.4.1*).

Plotting the depth of penetration of the samples against open porosity does not give any clear relationship between the two, even when minimum and maximum values are considered, as shown in Figure 9-1. This is also the case when compared to the gain in mass achieved in the samples by consolidation as shown in Figure 9-2. A similar plot against the capillary absorption coefficient suggests a weak relationship exists for it, more so in samples of high absorption, as shown in Figure 9-3.

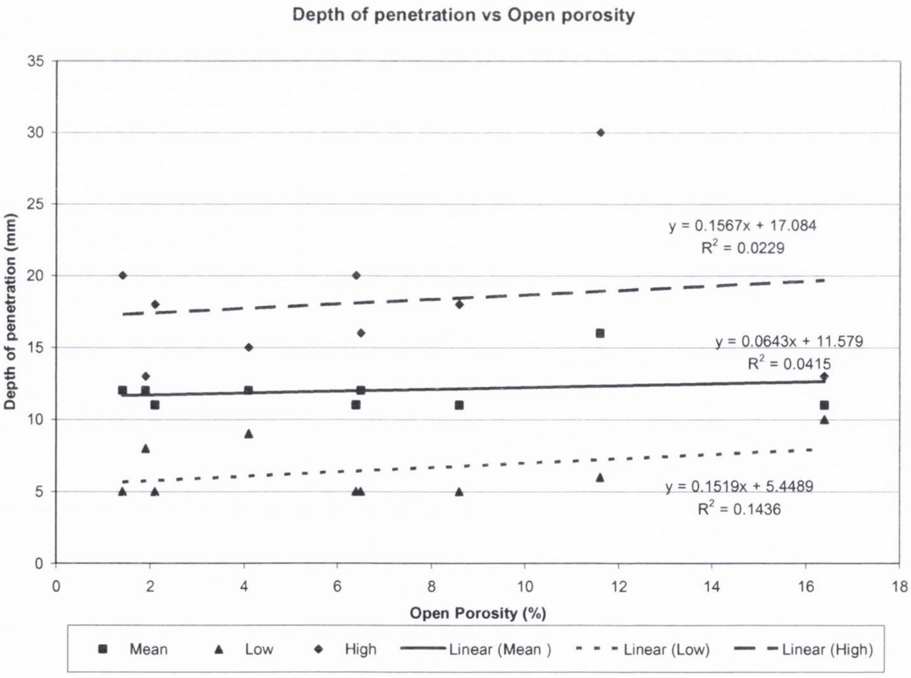


Figure 9-1: Depth of penetration determined for samples plotted against open porosity

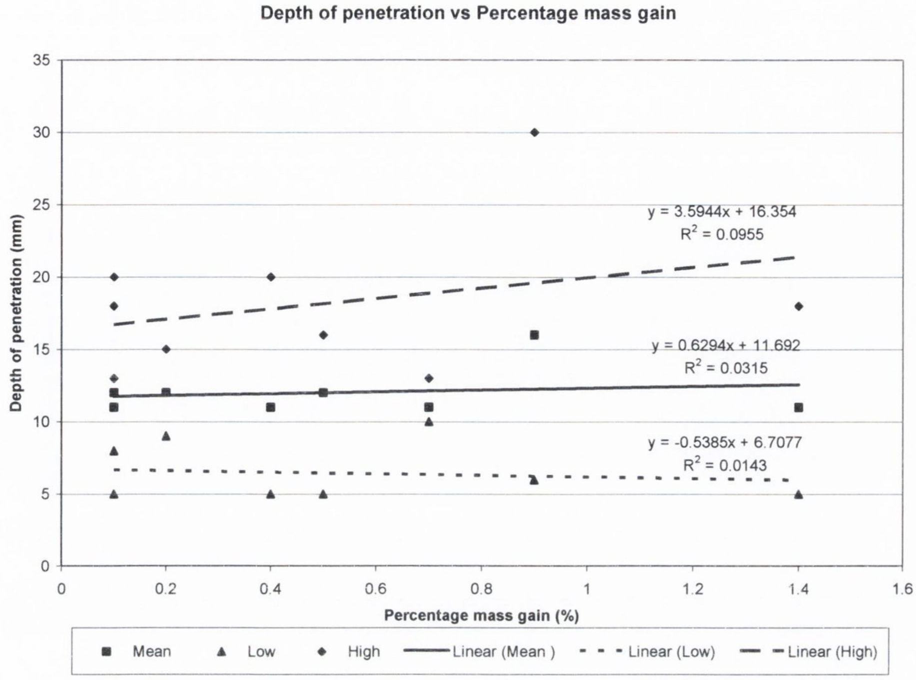


Figure 9-2: Depth of penetration determined for samples plotted against mass gain achieved

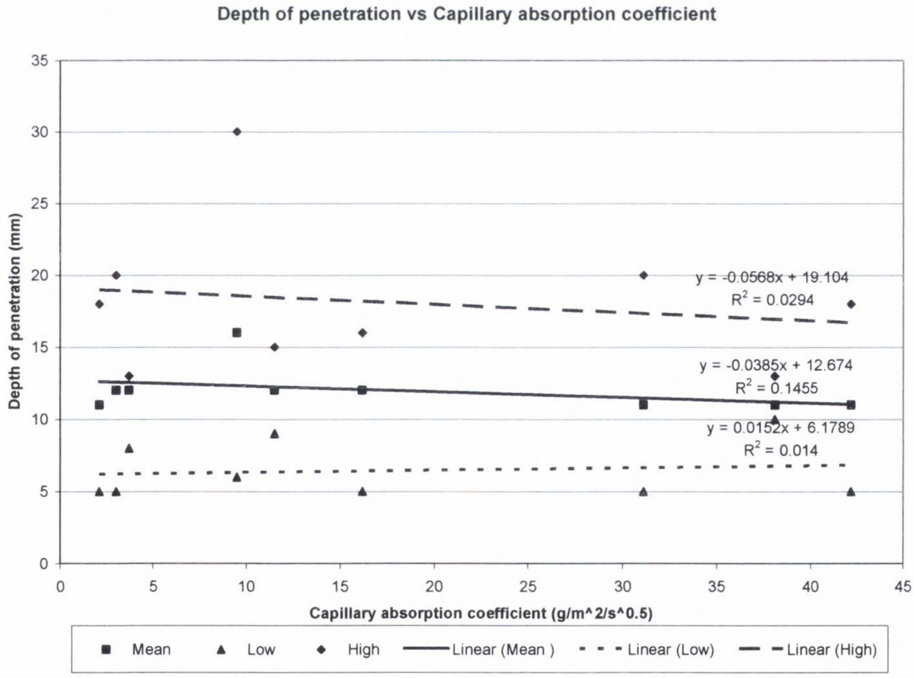


Figure 9-3: Depth of penetration determined for samples plotted against capillary absorption of application surface

If the depth of penetration is not proportional to mass structure properties and only weakly to capillary absorption, then what is it a primarily function of?

The Wacker-based consolidant treatments achieved marginally higher depths of penetration than the Tegovakon ones. This was shown in the results for both of the tests, as shown in *Section 6.4.2*. Similarly consolidant traces were suggested to be present at greater depths within the samples where solvents had been used. It may be assumed that both of these cases were due to lower liquid properties for viscosity and surface tension.

The results given in *Section 6.4.2.2 Surface wetting test* suggested that the TEOS products are highly likely to be absorbed preferentially along the top and bottom surfaces due to the influence of surface tension and pressure boundary conditions on capillary flow. This resulted in a low depth of penetration around surfaces, penetrating further along joints and fractures than through the sound substrate.

The depth of penetration is therefore less dependent on the sandstone properties and more strongly influenced by boundary conditions, atmospheric pressure in particular. The consolidants' surface tension and vapour pressure are primarily of greater importance than the properties of the stone, as consolidants spread easily across surfaces to minimise liquid pressure. Porosity and capillary absorption properties then have a secondary influence on the extent of absorption by capillary pressure. Continued application of the consolidant 'wet-in-wet' is thus necessary for penetration further into the stone. Appropriate solvent content can increase the likelihood of success in this respect.

9.3.2 Mass deposited and clear pores

Perhaps the mass of consolidant deposited is better related to the properties of the application surface? The mass gained was compared against the porosity of the application surfaces to investigate these relationships, as shown in Figures 9-4 and 9-5.

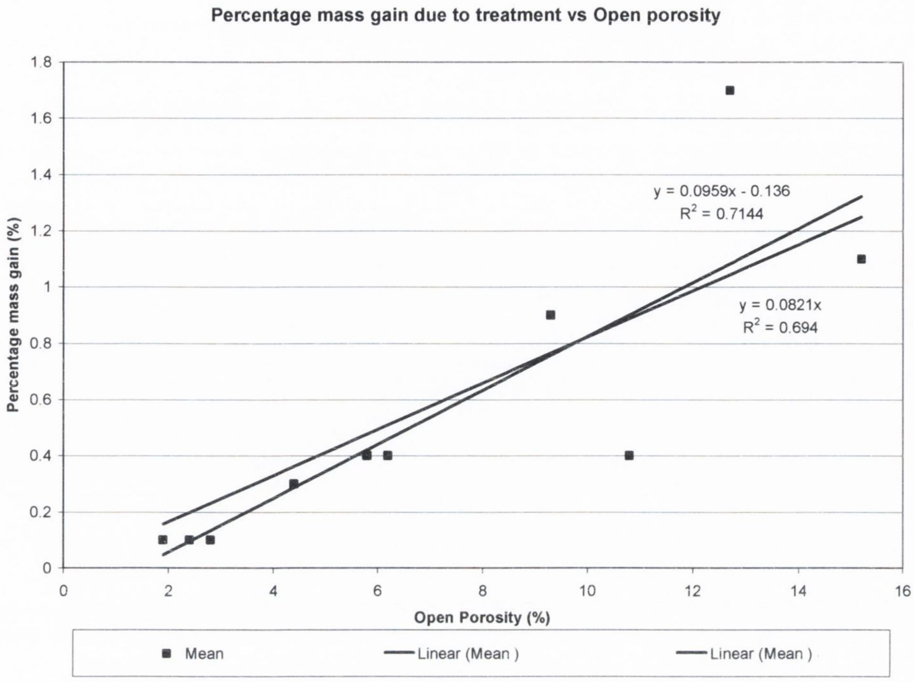


Figure 9-4: Gain in mass due to consolidation vs. open porosity of application surface, showing strong linear relationship for majority of samples

A direct linear relationship may be suggested between the open porosity of the application surface and the mass of consolidant deposited – its average slope is between approximately 0.082 and 0.096, but is not very accurate for samples of open porosity greater than 6%. The percentage mass deposited was slightly higher in samples treated with Wacker products than with Tegovakon ones. The maximum percentage mass gained was approximately 1.7%.

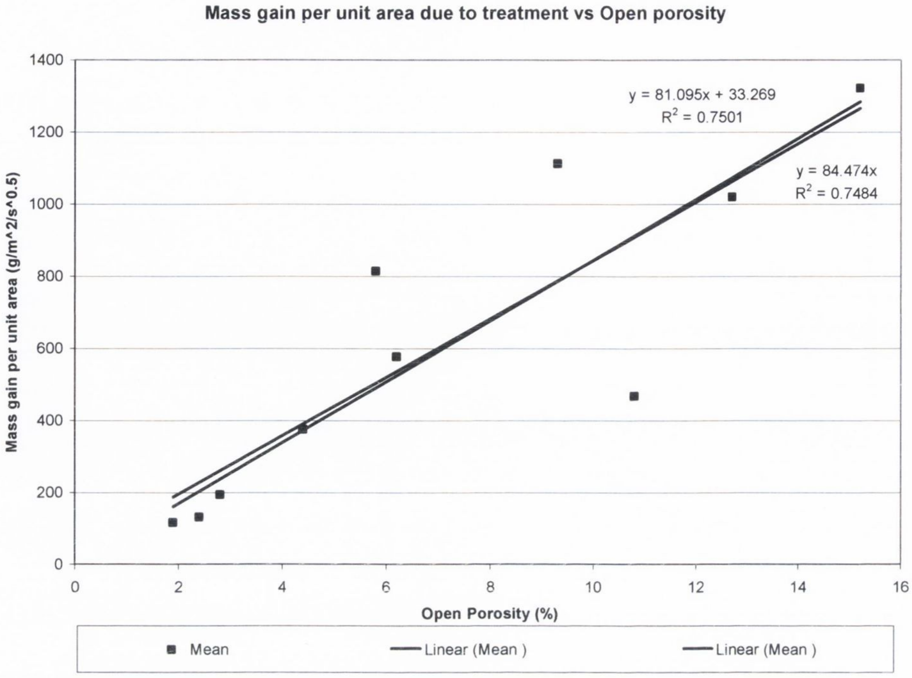


Figure 9-5: Gain in mass per unit area due to consolidation vs. open porosity of application surface, showing strong linear relationship for majority of samples

The relationship between the mass deposited by consolidant treatment per unit area and open porosity is better than the one for percentage mass gain. It increases at a slope of approximately 85*|Open porosity|*100 g/m^2. This relationship is better balanced, but is based on data with wide variations in open porosity, particularly in samples where porosity is greater than 6%.

As presented in *Section 6.4.1.2* the addition of the solvents to the Wacker consolidant did not result in greater mass deposition in the samples. It did for the Tegovakon consolidant however (Table 6-17). Perhaps the addition of the solvent was responsible for this increase? The absolute reduction from its slightly higher viscosity would be greater as a result of its lower percentage TEOS. It may then be absorbed into the samples in greater quantity.

Based on the percentage mass increases achieved by treating the samples and average sample density and dimensions, it can be shown that consolidation entailed an increase of between 0.8 and 1.1 kg/m^3. Using comparable values for sandstone's specific surface area (Franzen & Mirwald, 2004) it was estimated that the consolidant film deposited in treated samples was between 0.6μm and 0.8μm thick on average. Simple calculations also suggest that the average pore size of the samples should be in the range of 3-4μm. The likelihood of pore blockages occurring is therefore much less than 1:2 depending on the pore size distributions of the samples.

9.3.3 PMC's: bonding gaps and blocking pores

As mentioned in *Chapter 8* the durability of the samples to which the different consolidant treatments were applied varied. The results presented in *Section 6.4.1.3* (p.107) for the modulus of elasticity of weathered (untreated) and treated samples were also influenced by these variations in sample durability.

It was shown that PMC treatments applied to sparsely cemented samples improved the modulus of elasticity significantly. This was despite greater losses having previously occurred in them, i.e. decay was at a more advanced stage. The sizes of the interparticle gaps caused by flaking and granular disintegration would be of the order of the maximum that may be bridged by TEOS in these samples. Hence it may be assumed that PMC's can increase the maximum gap that may be bonded by TEOS consolidants.

When PMC treatments were applied nanoparticle flocs agglomerated in the outer layers of the sandstone surface and substrate. They were deposited from the TEOS solution, which then penetrated further into the stone, even if inhibited. The TEOS gelled around the deposited agglomerations, thus forming a thicker blanket in the pores depending on concentration. This modified gel also cracked due to the differential stresses caused during solvent evaporation. It had a much higher capacity to withstand the stresses than the separate TEOS gel however.

The porosity of samples treated with PMC's was reduced by approximately 29.0% on average, much greater than the changes due to the other treatments. These ranged in magnitude from 3.4% to 8.1% for the TEOS and TEOS+MEK treatments. This difference was most noticeable in the Manorhamilton samples because of its open porosity.

The agglomerations pack in some of the gaps, allowing the consolidant to bridge the distance between grains. These agglomerations are limited to the outer surface, precisely where the grains are least cohesive and the gaps are largest. PMC's are therefore more suitable where a surface is in an advanced stage of granular disintegration or flaking. The losses that may have been deemed sacrificial but necessary so that consolidant treatment may better protect the substrate ought to be lower if PMC treatments are applied.

Sponging of the surface with solvent after application did little to remove agglomerated material. As a result the whitish PMC gel affected the appearance of the stone considerably, particularly where the surface was roughest. The nanoparticles should therefore not be applied to the surface once it is observed that they are accumulating on it. Applying TEOS or solvent solutions after initially applying PMC solutions may reduce the effect that this on the surface appearance, or gradually rinse them into the pores. To overcome the issues of aggregation of the particles there are several steps that should be taken, most referring to Aggelakopoulou *et al* (2002):

1) Use either larger diameter oxide nanoparticles (e.g. 300nm) with 10nm silica for steric stabilisation, or else use only 10nm silica, as the particles sizes used in previous PMC studies are much more compatible due to the higher size ratios
2) Use a much lower volume percentage of nanoparticles to decrease the probability of collisions and hence of agglomeration occurring to such a scale
3) Ensure that the number of the smaller size nanoparticles is less than the number of larger size nanoparticles
4) Disperse the nanoparticles in Isopropanol by mixing with ultrasonic pulsing: the combination of the PUNDIT ultrasonic velocity apparatus with a suitable container may be practical and suitable for field use. An ice bath may be required to control the temperature. Then add in the TEOS and mix again.
5) Avoid applying any large flocs to the surface

Chapter 10:

Discussion

Effects of treatment on breathing ability of sandstone

10 Discussion: Effects of treatment on breathing ability of sandstone

If the outer porosity of sandstones were blocked by the nanoparticle agglomerations of the PMC treatments to what degree was the evaporation of moisture impeded? How do the effects of these blockages relate to the changes effectuated by treatment with non-PMC consolidant treatments? What effect does treatment have on moisture transfer properties and how does it alter pore interconnectivity?

In order to answer these questions it is necessary to relate the mass structure and moisture transfer properties and assess the differences between unweathered, weathered and treated samples during moisture transfer:

10.1 Correlation between mass structure and moisture transfer properties

The relationships between the mass structure and the moisture transfer properties were analysed to assess the degree of interconnectivity in the pores. Comparisons between these properties for the unweathered, weathered and treated states of the samples demonstrated whether treatment had affected it excessively or not.

The intercept and slope of the plotted line for capillary absorption or evaporation vs. open porosity were calculated. This gives a linear relationship of $y = B + C*x*100$, where the units of the constants B and C are $g/m^2/s^{½}$ for absorption (as in *Section 10.1.1*) or $g/m^2/hr$ for evaporation (as in *Section 10.1.2*).

These allow direct quantitative comparisons to relate the two mutually dependent properties that are illustrative of the pore characteristics.

10.1.1 Capillary absorption

The capillary absorption coefficient of the unweathered, weathered and treated sandstones is compared in Figures 10-1 and 10-2:

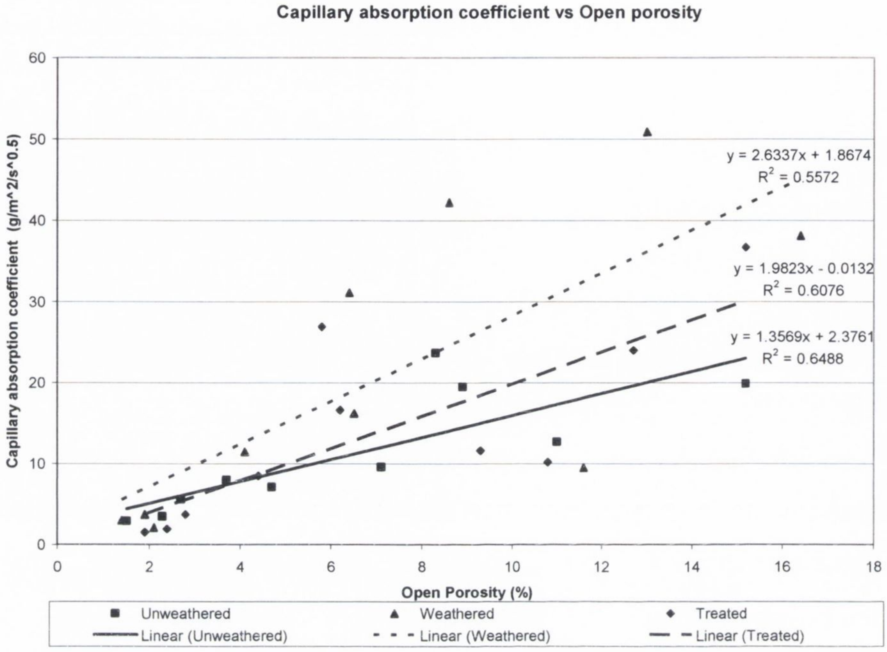


Figure 10-1: Plot of capillary absorption coefficient, C_{exp} against porosity, showing the averages for the unweathered, weathered and treated samples

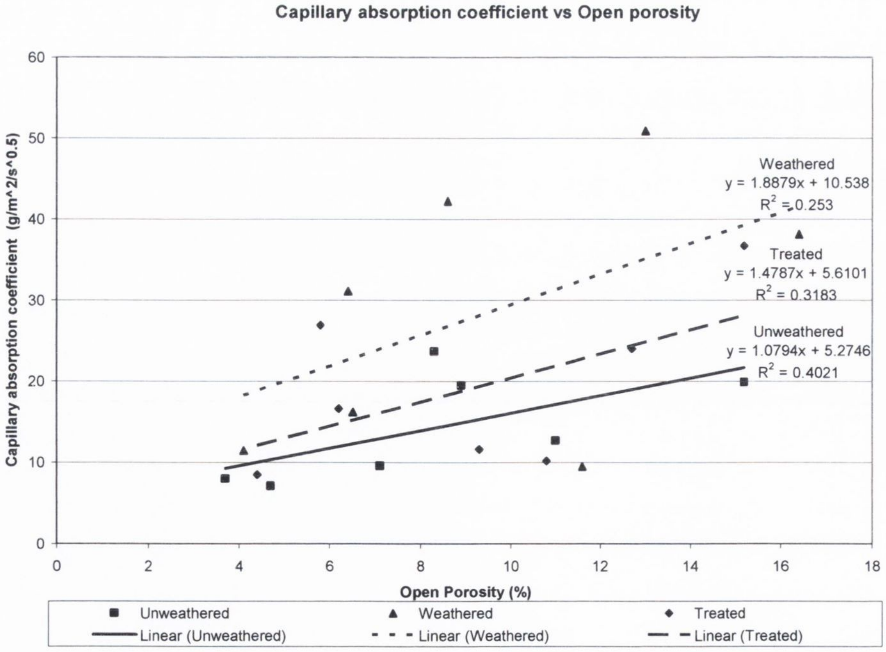


Figure 10-2: Plot of capillary absorption coefficient, C_{exp} against porosity, showing the averages for the unweathered, weathered and treated samples (Killaloe samples omitted)

The inclusion of the least porous samples is observed to significantly affect the correlations of capillary absorption coefficient and open porosity. By comparing the trend-line intersection values, it can be seen that their inclusion causes a skew towards lower values, or from the other viewpoint, their omission causes a skew towards higher values. The variance of the weathered samples was greater than for the unweathered and treated ones.

On average, the capillary absorption coefficient of the weathered sandstone was greater by |0.95*Porosity| $g/m^2/s^{\frac{1}{2}}$ when compared to the unweathered. When treated it was reduced on average by an absolute amount of |0.25*Porosity| $g/m^2/s^{\frac{1}{2}}$, compared to the weathered. Hence the change caused by consolidant application was generally between 5 and 10 $g/m^2/s^{\frac{1}{2}}$.

Further comparisons are made for the capillary absorption of the samples over longer time periods in Figures 10-3 and 10-4 on the following pages. These show that after much higher initial capillary absorption, its continued progress over subsequent 24-hour periods is generally reduced by weathering.

Converse shifts in moisture absorption are observed following treatment of the samples. Where it has been reduced in earlier periods, absorption may continue for longer at a relatively higher rate.

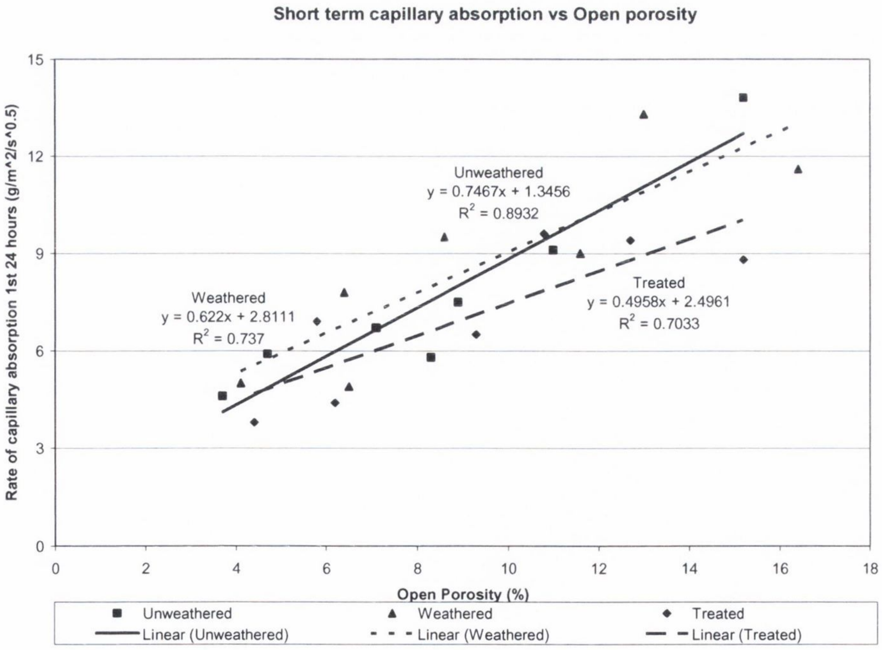


Figure 10-3: Plot of short-term capillary absorption against porosity, showing the averages for the unweathered, weathered and treated samples (Killaloe samples omitted)

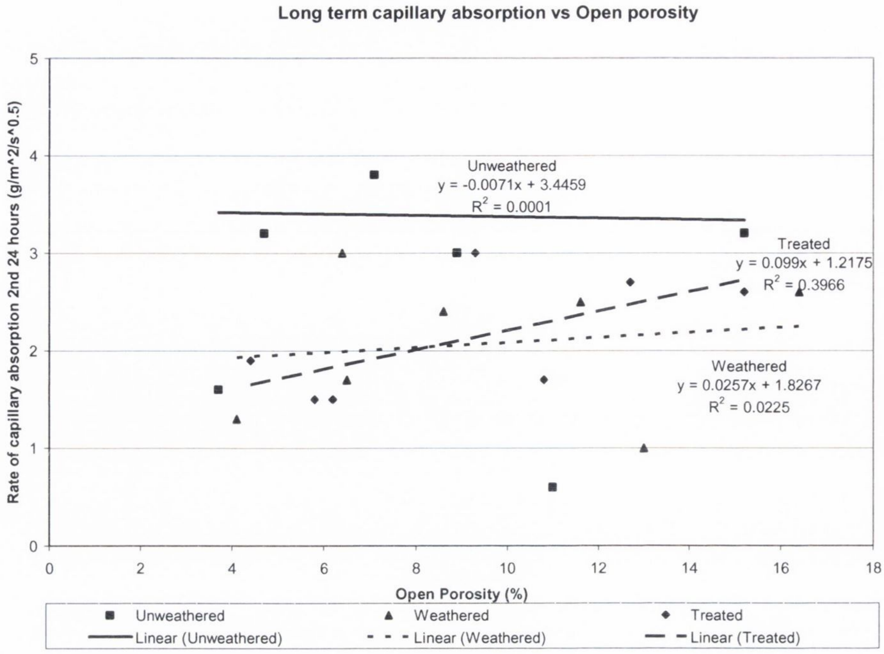


Figure 10-4: Plot of long-term capillary absorption against porosity, showing the averages for the unweathered, weathered and treated samples

The crux of these combinations is that weathered sandstone absorbs moisture much more quickly, and treated sandstone absorbs moisture much more slowly.

10.1.2 Evaporation

The evaporation of moisture from the unweathered, weathered and treated sandstones is compared in Figures 10-5 and 10-6:

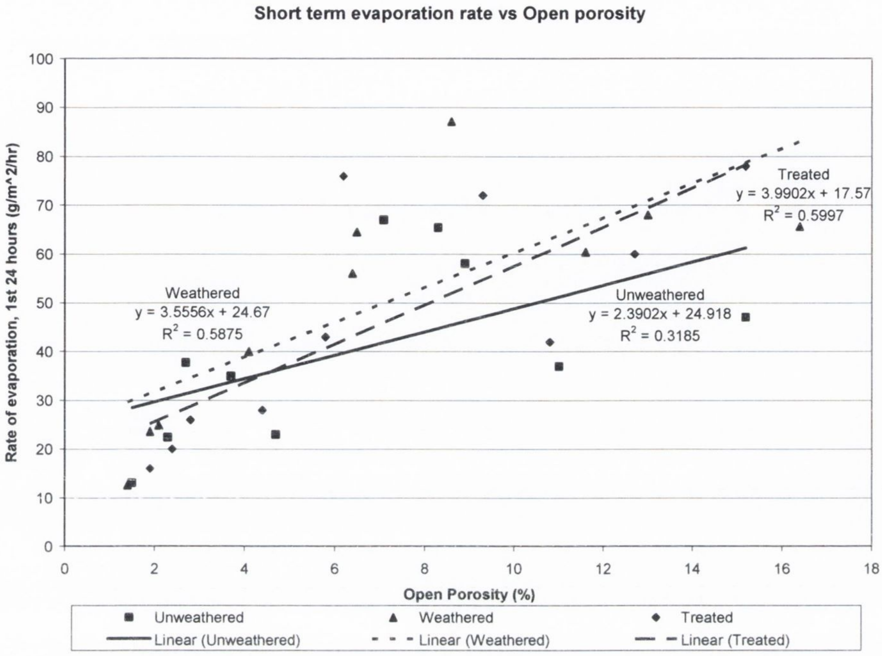


Figure 10-5: Plot of short-term evaporation against porosity, showing the averages for the unweathered, weathered and treated samples

Evaporation rates over 24 hours were increased by approximately |1.1*Porosity| g/m^2/hr due to weathering in most of the samples, bar those of low porosity. Treatment decreased the rates by up to 7.5 g/m^2/hr in the low porosity samples, although the rates in the medium-high porosity samples remained relatively unchanged.

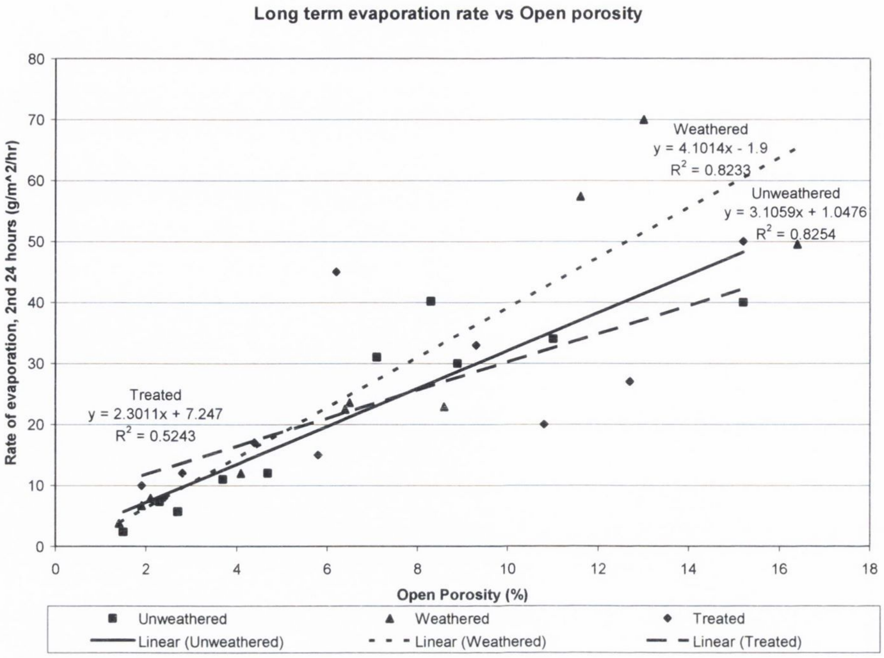


Figure 10-6: Plot of long-term evaporation against porosity, showing the averages for the unweathered, weathered and treated samples

Weathering increased evaporation during the 2nd 24-hour period in medium- high porosity samples only. Following treatment these reduced by between 1/6th and 1/3rd, returning to the unweathered levels or even slightly lower.

Treatment caused the rates in low porosity samples to increase by no more than approximately 5 g/m^2/hr. This would almost double the rate for some samples of low porosity.

It is noticeable from the graph that the correlation is somewhat skewed however. On inspection it is primarily the Killaloe dark grey sample that is at fault (6.2%, 45 g/m^2/hr).

The increase in the long-term evaporation of the low porosity samples was perhaps due to the reduction in the evaporation over the short term. This could possibly mean that more moisture is retained for longer in treated samples.

The degree of saturation in the samples should be analysed to factor out any mass structure effects from these correlations. This should verify if the proportion of moisture is held for shorter or longer durations as a direct result of the changes in porosity caused by weathering and treatment.

10.2 Analysing the percentage saturation during moisture transfer to assess breathing ability

10.2.1 Calculation of the percentage saturation during moisture transfer

As described in *Section 10-1* the porosity and moisture transfer of the samples are generally reduced by treatment, however the balance of moisture present in low porosity samples appears to be higher for longer as the long-term evaporation rates were increased. This should also be reflected in the percentage saturation of the samples. This is the percentage of moisture present in the pore volume of the samples, as calculated by Equation [3] in *Section 5.2.2.1.* This is more easily compared between the unweathered, weathered and treated states for the samples as it is based on the actual pore volume in each condition, not the rate of transfer. The percentage saturation influences the progress of moisture dependent processes relating to decay such as mineral dissolution, for example.

The profiles for the percentage saturation during capillary absorption and evaporation of each sample in the unweathered, weathered and treated conditions are presented in Appendix 10-A. Shown for each sample are profiles of:

a. the capillary absorption and evaporation curves, as calculated from the tests and reported previously,

b. initial capillary absorption (up to 8 hours), after which time the saturation is calculated as described in the following paragraphs:

Starting from the dry condition, the saturation increases exactly as for the capillary absorption. When sufficient moisture is present the probability of evaporation processes occurring increase. The rates of evaporation derived during testing generally show that at lower saturations, capillary absorption ought to exceed evaporation considerably. The saturations increase towards an imagined ‘cross-over point’ – the saturation and time where the capillary absorption and evaporation curves are equal.

Assuming that the rates of moisture transfer (for both capillary absorption and evaporation) are effectively functions of saturation, their progress may be approximated by simultaneously combining their contributions according to the level of saturation over a defined time period. Saturation then increases or decreases according to the difference between the two rates. Following further progression the rates may change, in which case a further iteration is required.

When calculated over sufficiently small time periods the estimates approximate to the equilibrium saturation present in a monument at a point close to the source of moisture and also close to a surface through which evaporation may occur.

The percentage saturation in the samples after 48 hours of absorption and evaporation are compared in Table 10-1 on the next page.

10.2.2 Assessment of breathing ability

To assess the effects of weathering and treatment on the breathing ability of the sandstones there are several aspects that may be considered:

- The importance of capillary absorption in facilitating increases in the amount of moisture present
- The proportion of moisture remaining after sufficient periods of evaporation
- The long term or equilibrium moisture content in the stone if constant absorption and evaporation are permitted, e.g. near surface close to groundwater

Saturation Sample	after 48hrs Capillary Absorption (%)			after 48 hrs Evaporation (%)			Calculated at 48 hrs by Iteration (%)		
	U	W	T	U	W	T	U	W	T
Drumbane Grey	82	98 *+20%*	53 *-46%*	29	43 *+48%*	48 *+12%*	51	75 *+48%*	62 *-17%*
Drumbane Rusty (Cubes)	83	99 *+19%*	60 *-39%*	25	20 *-20%*	56 *+180%*	75	80 *+7%*	70 *-13%*
Drumbane Rusty (Prisms)	70	100 *+43%*	44 *-56%*	22	42 *+91%*	58 *+38%*	50	82 *+64%*	51 *-38%*
Manorhamilton	55	59 *+7%*	62 *+5%*	67	46 *-31%*	43 *-7%*	53	50 *-6%*	50 *-1%*
Clara Hill Grey	73	78 *+7%*	84 *+8%*	61	45 *-26%*	52 *+16%*	68	61 *-11%*	58 *-5%*
Clara Hill Yellow	67	103 *+54%*	50 *-51%*	64	38 *-41%*	58 *+53%*	50	60 *+20%*	58 *-3%*
Killaloe Buff	80	84 *+5%*	52 *-38%*	34	27 *-21%*	47 *74%*	49	56 *+14%*	51 *-8%*
Killaloe Grey-Green	87	95 *+9%*	68 *-28%*	42	39 *-7%*	32 *-18%*	75	70 *-7%*	58 *-17%*
Killaloe Ochre	82	82 *0%*	49 *-40%*	41	17 *-59%*	47 *+176%*	48	60 *+23%*	55 *-8%*
Killaloe Dark Grey	71	75 *+6%*	58 *-23%*	20	35 *+75%*	38 *+9%*	57	49 *-12%*	49 *0%*

Table 10-1: Percentage saturation in unweathered, weathered and treated samples after 48 hours of capillary absorption and evaporation. Also shown are those obtained by iterations based on the calculated rates of capillary absorption and evaporation as functions of saturation content

After 48 hours of capillary absorption the percentage saturation was generally greatly reduced, although this was not the case for either the Manorhamilton or Clara Hill Grey samples. The saturation in these two was increased, however the magnitude of the changes were the lowest at +5% and +8% respectively. In the case of the former it is understandable since the rate of capillary absorption was also one of the only increases measured following treatment. It can only be assumed that the increase in the saturation of the latter was as a result of changes to the porosity, its interconnectivity being perhaps the most likely factor. Following the weathering the Clara Hill Grey samples became more open due to fracturing. The gaps caused by fracturing are not sealable by TEOS consolidants, hence the porosity of the stone was reduced, but the volume in the fractures was not.

After 48 hours of evaporation the percentage saturation of the samples was generally increased, although this was not the case for either the Manorhamilton or Killaloe Grey-Green samples. The high open porosity of the former may have caused the progressive decreases in saturation following both weathering and treatment. Similarly, in the case of the latter it seems to have been the significant increase in open porosity following treatment that results in the lower value.

Following the calculation of the equilibrium saturation (by iterating the difference between absorption and evaporation rates as a function of saturation), it was observed that in the majority of samples it tends to increase following weathering and decrease following treatment. In the Manorhamilton, Clara Hill Grey, Killaloe Grey-Green and Killaloe Dark Grey samples there was a reduction in this equilibrium saturation following both weathering and treatment, most likely due to the combination of changes discussed above. It is possible that salts present in the pores after weathering had an effect on these results.

This suggests that the treatment of sandstones with consolidants reduces the equilibrium saturation levels of moisture for the conditions considered here. This is due to a combination of the changes in mass structure and moisture transfer brought about by lining the pores with consolidants. Although the magnitude of some of these changes may be very small, increases in equilibrium saturation due to treatment are not anticipated based on these findings.

Chapter 11:

Discussion

Stresses between treated and untreated layers in samples

11 Discussion: Stresses between treated and untreated layers in samples

As discussed in *Section 3.1.4.4* thermal expansion differences can cause magnified stresses due to large differences in mineral sizes leading to insolation weathering of the surface. Consolidant treatment has been known to cause sufficient variations in material properties to cause similar differential stresses. This is primarily linked to differences in the modulus of elasticity of the stone where the treated surface layer meets the untreated stone below the depth of penetration, as discussed in *Section 3.2.4.1.* If high temperature differentials occur this may lead to considerable surface losses by scaling, signifying the ultimate in treatment failure.

To assess the effects of treatment on the sandstone samples the mechanical strength properties and the depths of penetration achieved were analysed further.

11.1 Correlation between mass structure and mechanical strength properties

A plot of the compressive strength against apparent density for the samples demonstrates clearly those which have high relative strength, as shown in Figure 11-1:

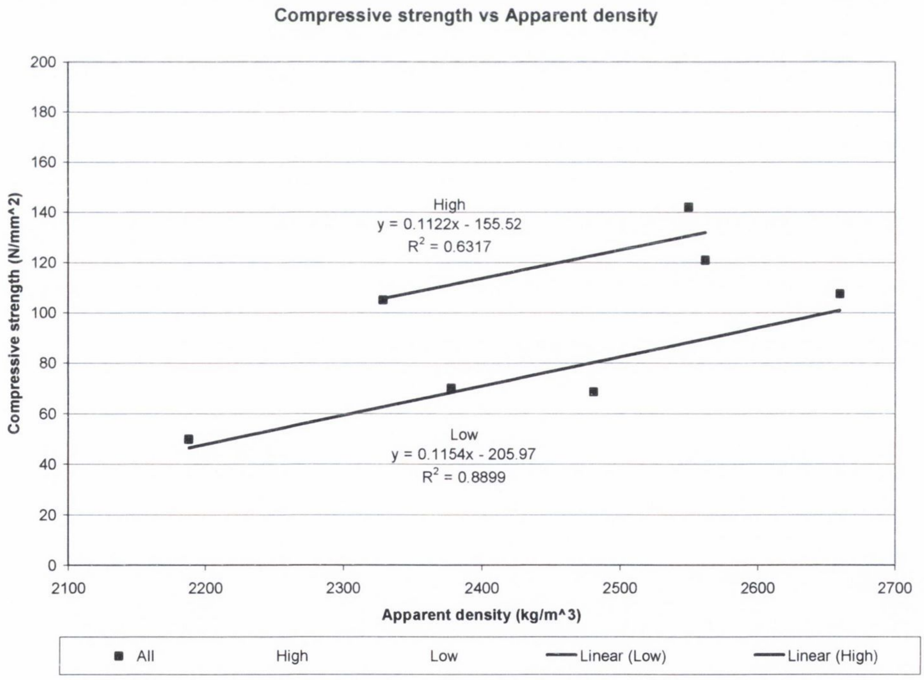


Figure 11-1: Plot of compressive strength vs. apparent density showing those above and below the relative average

The Killaloe Buff, Drumbane Grey and Manorhamilton samples have high compressive strength relative to their density. The Clara Hill Grey sample had the lowest compressive strength relative to its low-medium porosity.

When the values for the modulus of elasticity of the samples were plotted against density the Clara Hill Grey sample could also be distinguished as having well below average modulus for its density, as shown in Figure 11-2 (2480 kg/m^3, 17.9 GPa).

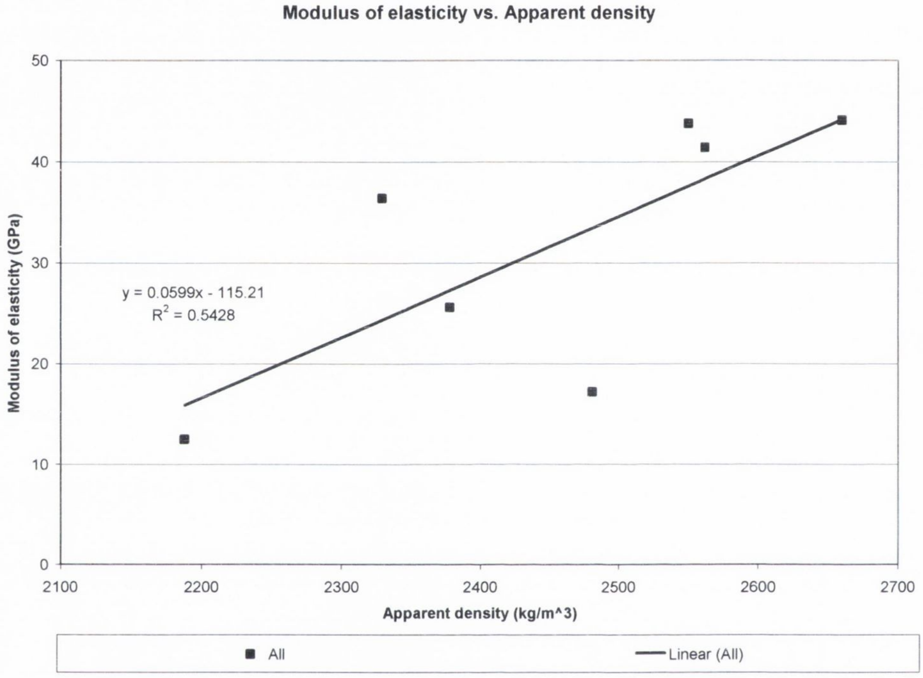


Figure 11-2: Plot of modulus of elasticity against apparent density

These correlations highlight that if treated, the Clara Hill Grey sample would be more vulnerable to insolation stresses than the other samples.

11.2 Analysis of maximum thermal stress/strain tolerable in samples

Thermal differential stresses may occur due to direct sunlight. Other conditions that may occur include a cool breeze causing heat loss from the surface on a hot summers' day for example. A difference between surface and subsurface temperatures of greater than 10 °C would be most unlikely in the Irish climate, as discussed in *Section 4.1.*

The linear thermal expansion coefficient of sandstone is assumed to be up to 12 μm/m/°C causing a strain of approximately $120*10^{-6}$ for such a thermal gradient, given that $\varepsilon = \alpha.\Delta T$ (McGreevy et al. 2000).

The maximum tensile strain that can be tolerated by the unweathered sandstones may be calculated using Equation [2] from *Section 5.2.2.2*. These results are presented in Table 11-1, assuming that tensile strength is approximately one tenth of compressive strength:

Sample	Modulus of elasticity (GPa)	Tensile strength (N/mm^2)	Corresponding max strain ($*10^{-6}$)	Max thermal gradient (°C)
Drumbane Grey	32	12.1	378	31.5
Drumbane Rusty	26	7.0	269	22.4
Manorhamilton	36	10.5	292	24.3
Clara Hill Grey	22	6.2	413	34.4
Clara Hill Yellow	13	5.0	385	32.1
Killaloe Buff	47	15.6	332	27.7
Killaloe Grey-Green	32	10.8	338	28.1

Table 11-1: Maximum strain and thermal gradient prior to tensile failure of unweathered sandstone samples, based on the available values for modulus of elasticity and assumed tensile strengths

This shows that the unweathered Drumbane Rusty and Manorhamilton sandstones are most at risk to insolation stresses, but can comfortably accommodate the temperature gradients likely to occur in Irish monuments.

Similar calculations are presented in Tables 11-2 and 11-3 for the weathered and treated sandstones, where the necessary data is available.

Sample	Modulus of elasticity (GPa)	Tensile strength (N/mm^2)	Corresponding max strain (*10^{-6})	Max thermal gradient (°C)
Drumbane Grey	31	9.7	303	25.3 *-20%*
Drumbane Rusty	12	-	-	-
Manorhamilton	21	4.1	195	16.3 *-33%*
Clara Hill Grey	-	-	-	-
Clara Hill Yellow	-	-	-	-
Killaloe Buff	43	10.0	233	19.4 *-30%*
Killaloe Grey-Green	33	14.0	424	35.4 *+26%*

Table 11-2: Maximum strain and thermal gradient prior to tensile failure of weathered sandstone samples, based on the available values for modulus of elasticity and assumed tensile strengths

Sample	Modulus of elasticity (GPa)	Tensile strength (N/mm^2)	Corresponding max strain (*10^{-6})	Max thermal gradient (°C)
Drumbane Grey	34	12.1	356	29.7 *+17%*
Drumbane Rusty	21	-	-	-
Manorhamilton	28	5.7	204	17.0 *+4%*
Clara Hill Grey	22	-	-	-
Clara Hill Yellow	22	-	-	-
Killaloe Buff	38	9.4	247	20.6 *+6%*
Killaloe Grey-Green	40	15.3	383	31.9 *-10%*

Table 11-3: Maximum strain and thermal gradient prior to tensile failure of treated sandstone samples, based on the available values for modulus of elasticity and assumed tensile strengths

Due to variability and lack of data available, the Killaloe Ochre and Killaloe Dark Grey samples are not examined. Data for the Clara Hill samples is also lacking.

The maximum thermal gradient tolerable was altered by between 10% and 30% for the weathered samples, with decreases occurring most often. There was an increase of 26% from 28.1°C to 35.4°C in the Killaloe Grey-Green sample. The weathered samples most at risk (for which sufficient information is available) are the Manorhamilton and Killaloe Buff sandstones.

The changes in these values brought about by treatment were much smaller. The greatest increase in maximum thermal gradient was +17% in the Drumbane Grey sandstone. The samples most at risk were only increased by 4% and 6% respectively.

Although the information is incomplete, it shows that in general:

- thermal insolation stresses do not pose excessive risk to sandstone in Ireland
- that weathered sandstone is at greater risk
- that treatment is likely to result in minor improvements

It should be noted that this analysis so far takes no account of the repeated action of thermal insolation stresses, whether in combination with other mechanisms or not, nor the effects due to the distribution of thermal stresses when applied to the outer surface.

11.3 Fatigue and thermal insolation stresses

The treated samples should have the capacity to withstand the tensile stresses caused by thermal differential stress. How long would it take for these stresses to cause fatigue and crack, allowing the outer treated surface to detach from the subsurface?

As with the values from Forgeron (2004) in *Section 3.1.4.5*, standard fatigue strength is generally specified as being the reduced strength after approximately 2 million stress cycles. 2 million cycles of diurnal thermal stress would take quite a while: even occurring twice a day it would take slightly under 2740 years. Brandt (1995) included a figure (*'Cement-based composites'*, p.296, Figure 11.9) that demonstrated a reduction of

25% in flexural strength (of plain concrete) after as few as 250,000 cycles, but even then it would take 342.5 years to happen if occurring only twice per day.

A 25% reduction in tensile strength in each of the unweathered, weathered and treated samples and the maximum thermal gradient are shown in Table 11-4:

Sample	Unweathered		Weathered		Treated	
	Tensile strength (N/mm^2)	Max thermal gradient (°C)	Tensile strength (N/mm^2)	Max thermal gradient (°C)	Tensile strength (N/mm^2)	Max thermal gradient (°C)
Drumbane Grey	9.1	23.6	7.3	19.0	9.1	22.3
Drumbane Rusty	5.3	16.8	-	-	-	-
Manorhamilton	7.9	18.2	3.1	12.2	4.3	12.8
Clara Hill Grey	4.7	25.8	-	-	-	-
Clara Hill Yellow	3.8	24.1	-	-	-	-
Killaloe Buff	11.7	20.8	7.5	14.6	7.1	15.5
Killaloe Grey-Green	8.1	21.1	10.5	26.6	11.5	23.9

Table 11-4: 25% reduction in tensile strength and maximum thermal gradient tolerable by the samples to allow for fatigue

However there are several differences between the concrete examples of Forgeron and Brandt and the sandstones:

- The former were subjected to live load cycles, not fluctuating thermal gradients.
- The latter have already been subjected to weathering, which will continue.
- Sandstones can have higher porosity than concrete due to low fine matrix content.

Hence micro-cracking is probably at a more advanced stage and crack propagation is thereby more likely to develop. This does not take into account the combined effects of thermal stresses, quartz dissolution, salt crystallisation or freezing-thawing.

The salt crystallisation tests have already been applied and presented, and it included temperature changes in the range of [20, 105] °C. Any thermal gradient induced in the samples when placed in the oven after salt immersion ought to be much different to that analysed above, since the samples are saturated with salt solution.

11.4 Analysis using results from a Finite Element Model for insolation stresses in treated stone (Hosek & Panek, 1985)

Using the depth of penetration and modulus of elasticity of the samples it was possible to determine stress coefficients for the interface between the treated and untreated layers, as calculated by Hosek and Panek (1985) (discussed in *Section 3.2.4.1*).

The model is based on the analysis of stresses in a stone element with two layers of properties. Their results are shown for ratios of the depths of the two layers (d_1/d_2), and ratios of their modulus of elasticity (E_1/E_2). The values in Table 11-5 are given, assuming a value of d_1/d_2 of 0.05, which is equivalent to a depth of penetration of 5mm or 10mm in a block of 100mm or 200mm depth respectively.

The stress coefficients and what they represent are shown in Table 11-5:

Stress coefficient	Represents the:
k_{xe}	Normal stress in the treated material at the exterior surface
k_{xs1}	Normal stress in the treated material at the depth of penetration
k_{xs2}	Normal stress in the untreated material at the depth of penetration
$k_{y,max}$	Maximum stress at the depth of penetration

Table 11-5: Explanation of the stress coefficients and what each represent, from Hosek & Panek (1985)

These are illustrated in Figure 11-3 on the next page. Also shown (in Table 11-6) are the stress coefficients obtained for the sandstone samples using their modulus of elasticity and the average depths of penetration as presented in *Chapter 6*.

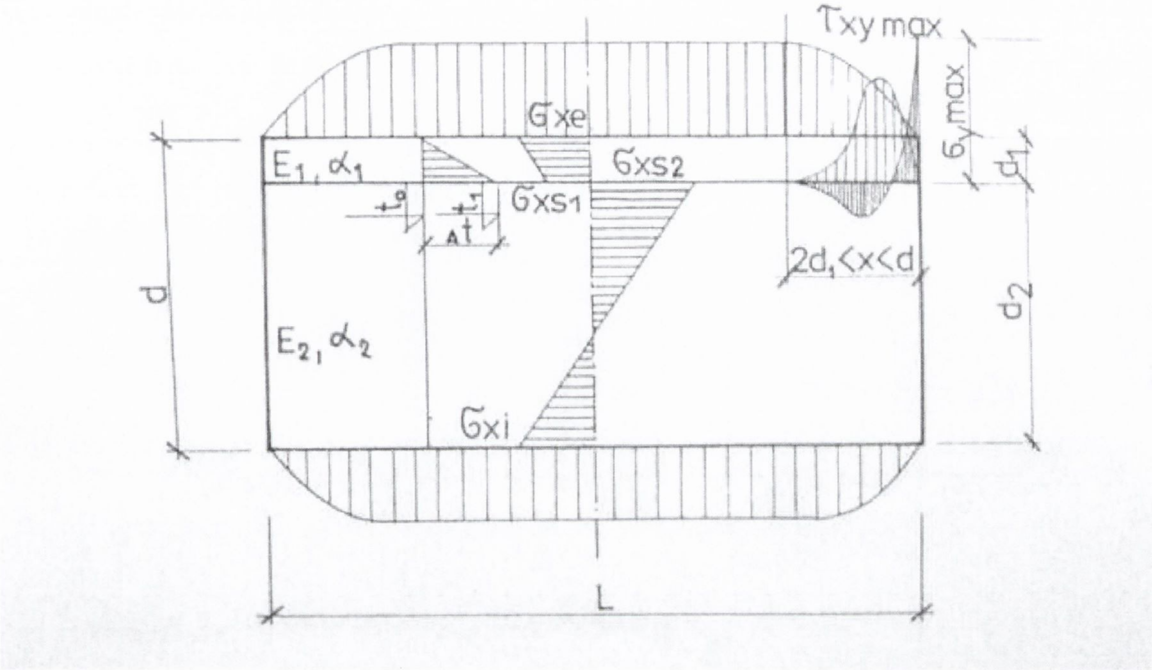


Figure 11-3: Stresses in a consolidated stone structure due to external temperature source, from Hosek & Panek (1985). The depth of penetration is d_1, the part at the top.

Sample	E_1 / E_2	Stress coefficients				
		k_{xe}	k_{xs1}	k_{xs2}	$k_{y,max}$	Δk_{xs12}
Drumbane Grey	1.1	0.53	0.70	-0.33	0.15	1.03
Drumbane Rusty	1.8	0.82	1.05	-0.39	0.23	1.44
Manorhamilton	1.3	0.70	0.82	-0.34	0.24	1.16
Clara Hill Grey	1.5	0.70	0.93	-0.37	0.10	1.30
Clara Hill Yellow	1.7	0.82	1.00	-0.38	0.25	1.38
Killaloe Buff	1.2	0.50	0.80	-0.34	0.15	1.14
Killaloe Grey-Green	1.3	0.60	0.85	-0.34	0.20	1.19

Table 11-6: Stress coefficients for interface between treated surface layer and unweathered subsurface material due to linear thermal expansion in tested samples, based on the results of Hosek & Panek (1985)

From the arrangement shown in Figure 11-3 it is observed that at the depth of penetration, the difference in the normal stresses of the treated and untreated layers is equal to $s_{xs2} - s_{xs1}$.

This shows that a thermal gradient in the stone would cause stresses to be 44% higher in the Drumbane Rusty and 38% higher in the Clara Hill Yellow samples at the depth of penetration, than if the stone were not treated. The Drumbane Grey, Manorhamilton and Killaloe Buff samples were affected the least, at 3%, 16% and 14% respectively. On average stresses were 23% greater at the depths of penetration due to insolation.

One other very noteworthy observation may be made: the highest values (generally greater than or equal to 1.30) are for the samples for which the required mechanical strength data is lacking. This data is not available because the samples were not suitable for crushing because of the effects of weathering. This only verifies that stone that is damaged more heavily by weathering is also more vulnerable to insolation stresses.

The obtained stress coefficients may be used to reduce the estimates for maximum tolerable tensile strain proportionate to this vulnerability, as shown in Table 11-7 on the next page. The reduced estimates for maximum thermal gradients are still greater than 10°C. It can be assumed that for the other samples it may be closer to or less than 10°C.

Sample	Max thermal strain ($*10^{-6}$)	Stress coefficients Δk_{xs12}	Reduced max thermal strain ($*10^{-6}$)	Max thermal gradient (°C)
Drumbane Grey	356	1.03	345	28.8
Drumbane Rusty	-	1.44	-	-
Manorhamilton	204	1.16	171	14.3
Clara Hill Grey	-	1.30	-	-
Clara Hill Yellow	-	1.38	-	-
Killaloe Buff	247	1.14	212	17.7
Killaloe Grey-Green	383	1.19	310	25.8

Table 11-7: Thermal strain and gradient of samples reduced in proportion to the stress coefficients calculated from the results of Hosek & Panek (1985). The stress coefficients are based on the depths of penetration and modulus of elasticity of the treated and underlying sandstone

11.5 Increased vulnerability to thermal stresses because of poor penetration of consolidant treatments

The calculation of these interfacial stresses as a result of thermal gradients provides an indirect way of assessing the risks associated with inadequate penetration of the consolidants. The results presented in *Section 11.4* are calculated here in Table 11-8 using the minimum range of values obtained for the depth of penetration:

Sample	E_1 / E_2	Stress coefficients				
		k_{xe}	k_{xs1}	k_{xs2}	$k_{y,max}$	$\Delta\ k_{xs12}$
Drumbane Grey	1.1	0.50	0.75	-0.33	0.11	1.08 *+5%*
Drumbane Rusty	1.8	0.60	1.60	-0.36	0.14	1.96 *+36%*
Manorhamilton	1.3	0.60	0.90	-0.32	0.09	1.22 *+5%*
Clara Hill Grey	1.5	0.50	1.30	-0.35	0.03	1.65 *+27%*
Clara Hill Yellow	1.7	0.80	1.10	-0.38	0.23	1.48 *+7%*
Killaloe Buff	1.2	0.32	0.90	-0.28	0.05	1.18 *+4%*
Killaloe Grey-Green	1.3	0.40	0.95	-0.30	0.20	1.40 *+5%*

Table 11-8: Stress coefficients for interface between treated surface layer and unweathered subsurface material due to linear thermal expansion in samples with low depth of penetration, based on the results of Hosek & Panek (1985)

The increase in these stress coefficients is remarkably higher if poorer penetration occurs. The increases are greatest in the two samples that had the worst fracturing following the artificial weathering, Drumbane Rusty and Clara Hill Grey.

Sample	Max thermal strain ($*10^{-6}$)	Stress coefficients Δk_{xs12}	Reduced max thermal strain ($*10^{-6}$)	Max thermal gradient (°C)
Drumbane Grey	356	1.08	327	27.3 -5%
Drumbane Rusty	-	1.96	-	-
Manorhamilton	204	1.22	159	13.3 -7%
Clara Hill Grey	-	1.65	-	-
Clara Hill Yellow	-	1.48	-	-
Killaloe Buff	247	1.18	202	16.9 -5%
Killaloe Grey-Green	383	1.40	230	19.2 -26%

Table 11-9: Thermal strain and gradient of samples with low penetration of the consolidant reduced in proportion to the stress coefficients calculated from the results of Hosek & Panek (1985)

The increased vulnerability of samples with low penetration of the consolidants to thermal stresses is bringing the tolerable thermal gradients closer to the range of values considered likely in Ireland. This must be assumed to be especially true in the sandstones for which data is lacking.

11.6 Geometric considerations of findings on penetration and thermal stresses

Unfortunately the difference between the dimensions of the tested samples and the dimensions of typical monumental elements does have a direct effect on the output from this analysis. Hence there may need to be an adjustment to be comparable to monumental conditions.

The d_1/d_2 ratio used above assumed d_1 = depth of penetration and d_2 = 25mm, the maximum depth of weathering in cubes of 50mm side. In historic masonry the depth of weathering in individual blocks may be greater than this.

The assumption that the depth of weathering is 25mm may not be accurate. It should be understood that where this is the case, consolidant penetration is much more likely to be close to the sound stone substrate, thereby reducing the perceived risk of such problems.

Chapter 12:

Discussion

Assessment of the compatibility of consolidant treatments with Irish monuments

12 Discussion: Assessment of the compatibility of consolidant treatments with Irish monuments

The effectiveness of consolidant treatments in improving Irish sandstone's resistance to weathering has been presented through the results and analysis. Their compatibility of the sandstones with the monuments, and hence their suitability, may now be determined using the characteristics from the petrographic studies and physical laboratory testing.

12.1 Compatibility of consolidant treatments with Irish sandstone

The compatibility of the treatments can be evaluated by calculating the 'Incompatibility Degree' performance indicator, as discussed in *Section 3.2.5*. This rates changes in each of the properties due to treatment to assess how appropriate a consolidant treatment is for a particular substrate.

The relevant risks, criteria and ratings are outlined in Table 12-1 on the next page, showing those variables that were measured in laboratory testing of the samples or analysed using selected results.

The rates are represented as (→ 10) in the text accompanied by an explanation.

Criteria	Compatibility indicators	Incompatibility risks	Rating
Chemical and mineralogical composition	Presence of carbonates	Absent Minor Significant	→ 0 → 5 → 10
	Presence of salts or biological growth	Absent Minor Significant	→ 0 → 5 → 10
	Presence of clays	Aiding cohesion None Easily weathered	→ 0 → 5 → 10
Mass structure and pore space	Gaps between particles losing cohesion	Minor Average Large	→ 0 → 5 → 10
	Interconnectivity of pores	High Medium Low	→ 0 → 5 → 10
	Pore sizes	Medium Fine Very fine	→ 0 → 5 → 10
Moisture transfer and breathing ability	Capillary absorption	= weathered-untreated > weathered-untreated	→ 0 → 10
	Evaporation	= weathered-untreated > weathered-untreated	→ 0 → 10
	Percentage saturation	= weathered-untreated > weathered-untreated	→ 0 → 10
Mechanical and thermal properties	Compressive strength	<10% 10-25% higher >25% higher	→ 0 → 5 → 10
	Modulus of elasticity	<10% 10-25% higher >25% higher	→ 0 → 5 → 10
	Risks posed by insolation stresses	Low Medium High	→ 0 → 5 → 10
	Depth of penetration	>20mm 5-20mm <5mm	→ 0 → 5 → 10
Durability and appearance	Change in appearance	Unnoticeable Noticeable + variations worse	→ 0 → 10
	Durability	> untreated = untreated	→ 0 → 10

Table 12-1: Suggested ratings for compatibility of TEOS consolidant treatments with weathered sandstone (NB: intended to be adjusted as appropriate – includes both overlaps and contradictions)

The suitability of consolidant treatment is discussed further in relation to the criteria in Table 12-1 for both overall and individual sample characteristics.

12.2 Chemical and mineralogical composition

Silanol bonding of some TEOS products may be compromised on basic carbonate surfaces, as discussed in *Section 3.2.2*. Of the four samples only the Killaloe Grey-Green one contains any carbonate minerals (<5%, minor → 5). TEOS ought to have a good affinity with the others' acidic nature due to quartz content (absent → 0).

The presence of salts or biological growth may also compromise the consolidants' ability to bond to the substrate (*Section 3.2.2*). The samples were washed thoroughly to remove the salt content after the artificial weathering. For the testing conditions salt and biological growths were removed (absent → 0).

Commercial consolidant products containing prehydrolysed and catalyst content often avoid such problems (depending on product → 0).

The presence of fine matrix was shown to be beneficial in *Section 8.6*, as it can aid cohesion in stone. Where it is present as clay content, provides little or no cohesive action or is weathered, the risks to durability and hence compatibility are higher. The application of PMC treatments can improve bonding between TEOS and the constituent grains if fine matrix is absent.

12.3 Mass structure and pore space

It is the pore characteristics, as discussed throughout *Section 3.1.2* and presented in *Section 6.1*, that influence the success of the consolidant treatments. Fine pores are more prone to becoming blocked due to TEOS' shrinkage mechanism during condensation. Medium pores are more likely to facilitate deeper penetration. Angular pores provide greater surface area for the consolidants to bond to, resulting in a thin film that spreads out more evenly. Fine or poorly distributed subspherical pores are more prone to becoming blocked due to TEOS' shrinkage mechanism during condensation. Modification of TEOS treatments with solvents can help penetration in stone of lower porosity or interconnectivity, as discussed in *Section 3.2.3.4*. They also reduce the likelihood of pore blockages as a thinner film is deposited.

Consolidant treatment with TEOS is less suitable where the gaps between particles are large however, as mentioned in *Section 3.2.2*. Decay types caused by weathering such as granular disintegration, flaking or fracturing correlate to varying cohesiveness and cementation, as described in *Section 8.6*. TEOS consolidants struggle to bond individual grains in the absence of fine matrix once cement connections have been broken. The application of PMC treatments can improve bonding between TEOS and the constituent grains, as demonstrated in *Section 9.3.3*. Pores were blocked by excessive agglomeration of high content PMC treatments.

12.4 Moisture transfer and breathing ability

The influence of moisture transfer on decay processes was discussed in *Section 3.1.4* and later in *Chapter 8*. Weathering generally increases capillary absorption in sandstone, drawing greater amounts of moisture from groundwater or rainwater sources. The ability of the stone to let such moisture evaporate is important, although excessive evaporation does correlate to decay by flaking. Treatment was observed to reduce the moisture transfer properties to values comparable with those of unweathered sandstone. In low porosity samples, they were reduced even lower however.

The percentage saturation reflects the degree of moisture available for decay processes that are held in stone. This was used to assess interconnectivity and possible pore blockages in *Chapter 10*. It was shown that almost all of the samples were better off after treatment as the calculated equilibrium levels were lower.

12.5 Mechanical and thermal properties

The effects of weathering and treatment on the mechanical properties of stone are mentioned throughout *Chapter 3*. Exposure of sandstone to weathering processes can cause gradual removal of cementitious minerals and the loss of cohesion between the other constituents. Strength and durability are compared as critical criteria for assessing consolidant efficacy in *Section 3.2.4.4*.

Weathering reduced both the compressive strength and modulus of elasticity considerably in some samples, even though the measurements were made on samples of better cohesiveness. High density sandstone maintained high levels in each, with almost immeasurable material losses. Consolidant treatment generally improved the mechanical properties, as presented in *Section 6.4.1.3.*

The effects of thermal stresses on treated sandstone were analysed in *Chapter 11*. The risks of fatigue due to insolation stresses were evaluated for each of the samples using FEM results and the depth of penetration and modulus of elasticity. The differences in temperature likely to occur in monuments subjected to direct sunlight in the Irish climate are thought to be less than 10°C. It was shown that the risks were highest in the two samples that happened to fracture the most during artificial weathering.

12.6 Durability and appearance

The durability of samples subjected to artificial weathering is widely used to evaluate consolidant treatment effectiveness, as described in *Section 3.2.4*. The results from the durability testing, as presented in *Section 6.4.4* and discussed in *Chapter 8*, clearly show that the treatments provide resistance to further weathering and decay. Samples of higher durability remained relatively unchanged whether treated or not.

Changes to the visual appearance of monuments requiring conservation are not desirable, as outlined in *Section 3.1.3*. Appearance is often reported to be relatively unchanged when alkoxysilane treatments are applied, as mentioned in *Section 3.2.4.1*. Consolidant treatments were observed to alter the appearance of some samples however, as discussed in *Sections 6.4.2* and *6.4.4*. Occasionally the difference was easily noticeable. In some cases variability within the stone made the effects either more or less noticeable. Occasional whitish marks left by agglomerated nanoparticles were easily distinguishable where PMC treatments were applied. On comparison, treated samples were in visibly better condition than untreated ones after further weathering.

12.7 Incompatibility ratings for the samples and monuments

12.7.1 Drumbane sandstone and Cormac's Chapel

12.7.1.1 Chemical and mineralogical composition

There are no salts present in Cormac's Chapel, however there is biological growth in the damp conditions of the east doorway (→ 10).

The clay matrix present in the pores of the Drumbane samples does add to its cohesive strength (Grey type → 0), but can be weathered away opening up the porosity (Rusty → 5).

12.7.1.2 Mass structure and pore space

The pores in the Grey type are fine-very fine and have lower pore interconnectivity (→ 10).

Some flaking of the material from the surface of the Grey samples was observed, resembling closely the blistering and flaking that is evident in the east doorway of Cormac's Chapel. The parts of the samples that displayed these effects contained local concentrations of clay and mica minerals. TEOS might not be able to stop outer surface losses depending on the condition and stage of weathering as flakes could continue to fall off if the gaps between grains are too great (→ 10). PMC treatments may therefore be more suitable from this point of view. Once the outermost weaker parts have fallen off the treated surface should have greater long term resistance to decay, assuming that the high moisture problems be addressed.

The pores in the Rusty type are medium-fine, but have a wide distribution and are highly interconnected (→ 0).

The west façade displays the same differential erosion and granular disintegration as the Rusty samples (→ 5).

12.7.1.3 Moisture transfer and breathing ability

The capillary absorption of the Grey type was reduced by treatment (→ 0). Evaporation was also reduced by treatment but remained in the medium range (→ 0).

Capillary absorption was reduced from high to medium in the Rusty type (→ 0). Evaporation remained high but was slightly less compared to the weathered-untreated samples (→ 0).

The percentage saturation calculated for the treated Grey samples was 17% lower than weathered-untreated samples (→ 0). For the Rusty samples it was 13% lower than the weathered one (→ 0).

12.7.1.4 Mechanical and thermal properties

Treatment of the Grey type may achieve penetration of between 9mm and 15mm according to weathering condition, with penetration being better along fracture planes and in areas of higher clay content (→ 5). The risks posed by insolation stresses to the Grey type were low (→ 0).

Penetrations are primarily in the range of 5-18mm in the Rusty type, depending on the severity of weathering (→ 5). In the Rusty type the risks posed by insolation stresses were high, confirmed by the occasional occurrence of fractures in the treated parts of the prisms (→ 10).

The compressive strength of the treated Grey samples was almost unchanged from the unweathered values (→ 0), and had been significantly improved compared to the weathered ones. Their modulus of elasticity was also increased by treatment, but was not greatly different (→ 0).

The modulus of elasticity of the Rusty type was increased by treatment, but was significantly higher in the treated cubes compared to the weathered-untreated ones (→ 5).

12.7.1.5 Durability and appearance

Comparison of the mass changes in the Grey type demonstrated that treated samples suffered half the weathering of untreated ones (→ 0). For the Rusty type the difference between the losses were even greater (→ 0).

The local variability and interjection of the two types suggest that the porosity levels do vary widely throughout the monument. Treated parts are noticeably darker when seen next to untreated parts in both types. There is already a marked difference in the monument after restoration works (Noticeable / Variations → 5).

12.7.2 Manorhamilton sandstone

12.7.2.1 Chemical and mineralogical composition

The Manorhamilton samples contained no clay matrix (→ 0).

12.7.2.2 Mass structure and pore space

The pores were fine-medium in size and subangular to angular in shape (→ 0). They were moderately sorted and had high interconnectivity (→ 0).

The weathering of the samples removed much material from the surface. Differential erosion occasionally resulted in details resembling carvings due to local weakness in the stone. The effects of flaking and granular disintegration were also frequent. This suggests that continued weathering progressively reduces the cohesion of the constituents and increases the gaps between them. Without any clay matrix content the bonding distance is likely to be quite large (→ 10). PMC treatments may therefore be more suitable where porosity is higher.

12.7.2.3 Moisture transfer and breathing ability

The capillary absorption was increased by the treatment but remained in the medium range (→ 10). Evaporation was increased in the short-term, but reduced in the long-term (→ 0). The percentage saturation calculated by iteration was relatively unchanged by both weathering and treatment (→ 0).

12.7.2.4 Mechanical and thermal properties

Weathering greatly reduced the compressive strength of Manorhamilton sandstone. It also increased their brittleness occasionally. Treatment produced varying results; some values were just as low as the weathered ones while others were either half or doubly replenished (→ 10). On average the strength of treated samples was improved compared to untreated ones.

Penetrations of between 6mm and 30mm were achieved in Manorhamilton samples. The risks posed by insolation stresses were medium (→ 5).

12.7.2.5 Durability and appearance

The treated samples lost lower amounts of material compared to the untreated ones during further weathering. PMC treatments may be more suitable because of the distances between particles (→ 0).

Manorhamilton sandstone contained a wide range of colours. Some of the samples had quite variable appearance due to varying iron oxide content. The presence of consolidants could not be noticed (→ 0).

12.7.3 Killaloe sandstone and St. Brendan's Cathedral

12.7.3.1 Chemical and mineralogical composition

Minor carbonate content was present in the Killaloe Grey-Green sample (→ 5).

Salt concentrations are present in the doorway at Clonfert however (→ 10).

The Killaloe sandstone contains little or no clay matrix (→ 0).

12.7.3.2 Mass structure and pore space

The pores in the Buff sample were very fine-fine (→ 10). They had medium pore interconnectivity (→ 5). For the Grey-Green sample they were fine-medium (→ 5), but had low pore interconnectivity (→ 10).

Most of the samples suffered only slight discolouration and opening of surface porosity due to weathering. There was very little loss of cohesion (→ 0).

12.7.3.3 Moisture transfer and breathing ability

The moisture transfer properties remained low after treatment. The rate of evaporation was similar to that of the unweathered stone (→ 0).

The percentage saturation calculated for the samples was lower after treatment. For the Buff and Ochre samples it was lower compared to the weathered samples (→ 0). For the other two samples it was also lower compared to the unweathered samples (→ 0).

12.7.3.4 Mechanical and thermal properties

On average the compressive strength and modulus of elasticity of the treated samples were only slightly lower than the unweathered values but some values were significantly higher after treatment (→ 5).

The depths of penetration in the Killaloe sandstone were between 5mm and 20mm (→ 5). The risks posed by insolation stresses were low (→ 5).

12.7.3.5 Durability and appearance

Both the treated and untreated samples absorbed a small amount of salts and lost very little material (→ 0).

The appearance was altered by treatment on the some of the samples, with a clearly distinguishable layer denoting the depth of penetration. The wide range of colours in the stone has already resulted in variations in the appearance of the monument (→ 10).

12.7.4Clara Hill sandstone and monuments at Clonmacnoise

12.7.4.1 Chemical and mineralogical composition

Both the Grey and Yellow samples contained clay matrix that provided some cohesion to the stone (→ 0).

12.7.4.2 Mass structure and pore space

The pores of the Grey type were fine in size (→ 5), and were poorly interconnected (→ 10).

Decay in the Grey type involved much fracturing, flaking and granular disintegration. The gaps between particles were observed to be relatively large (→ 10).

The pores of the Yellow type varied from coarse to fine in size and were angular in shape (→ 0). Pore interconnectivity was high (→ 0).

Granular disintegration and flaking occurred in the Yellow samples so consolidant treatment could have mixed results as the gaps between grains were also large (→ 10).

PMC treatments may therefore be more suitable.

12.7.4.3 Moisture transfer and breathing ability

The moisture transfer properties of both the Grey and Yellow samples remained high after treatment. They were both slightly lower compared to the weathered values (→ 0).

The percentage saturation of the Grey samples was 58%, lower compared to both the unweathered and weathered ones (→ 0).

The percentage saturation of the Yellow samples was 58%, lower compared to the weathered ones (→ 0).

12.7.4.4 Mechanical and thermal properties

The modulus' of elasticity of both the Grey and Yellow samples were much higher after treatment and were significantly different compared to both the unweathered and weathered ones (→ 10).

Consolidant penetration was measured to depths of between 5mm and 20mm in the Grey type (→ 5). The grey samples had the medium-high risk of damage due to thermal stresses. The whole outer surface of some cubes was removed during weathering due to a combination of salt crystallisation and thermal stress (→ 10). Consolidant penetration was measured to depths of between 5mm and 13mm in the Yellow type (→ 5). For the Yellow samples the risks were slightly lower, presumably due to its more open structure (→ 5).

12.7.4.5 Durability and appearance

Some of the Grey samples suffered massive losses during further weathering tests due to continued fracturing and crumbling of the weakened surfaces. Losses were much lower in the treated samples (→ 5).

There was no noticeable difference in appearance of Grey samples after treatment (→ 0).

Treatment reduced the rate of further weathering in the Yellow samples (→ 0).

The Yellow samples were noticeably darker when compared side by side with untreated ones. The PMC's managed to form a protective layer over the grains without becoming too noticeable (→ 5).

12.7.5Other sandstone in monuments at Clonmacnoise

Results and analysis are poorer for some of the sandstone in the monuments at Clonmacnoise. A few suggestions are made based on the environmental conditions and observations during fieldwork however:

12.7.5.1 Chemical and mineralogical composition

No salts were observed however occasional biological growth is present in the monuments (→ 5).

12.7.5.2 Mass structure and pore space

The granular disintegration in the Nun's Church and the Cathedral are quite similar. The gaps between the particles were not observed to be large (→ 0).

12.7.5.3 Moisture transfer and breathing ability

The monuments are situated in boggy lowlands on the banks of a major river (→ 10).

12.7.5.4 Mechanical and thermal properties

The decay effects seen in Temple Finghin at Clonmacnoise are more closely related to structural problems, with loading and movement effects responsible for much fracturing and the loss of detailed voussoirs. Unless remedial action is taken against further settlement the decay cannot be addressed by consolidation (→ 10).

12.8 Calculation of the Incompatibility Degree

The calculation of the Incompatibility Degree of the treatments with the samples or monuments is dependent on the risks chosen and the weighting appointed to each. They may be averaged simply or by using the quadratic mean. Certain ones may be omitted or even doubled as the individual sees fit. Several sample calculations are presented in the following tables to illustrate this, according to the criteria already set out in this chapter.

In Table 12-2 the risks were averaged for each of the compatibility indicators:

Rating / Criteria	Drumbane		Manorhamilton	Clara Hill		Killaloe	
	Grey	Rusty		Grey	Yellow	Buff	Grey-Green
Chemical and mineralogical composition	5	2.5	0	3.3	5	3.3	5
Mass structure and pore space	10	2.5	3.3	8.3	3.3	8.3	8.3
Moisture transfer and breathing ability	0	0	3.3	0	0	0	0
Mechanical and thermal properties	1.1	6.6	7.5	5	6.6	5	5
Durability and appearance	2.5	2.5	0	2.5	2.5	5	5
Incompatibility Degree	3.7	2.8	2.4	3.2	2.4	4.3	4.7

Table 12-2: Incompatibility Degree calculated for the treatment of the samples and monuments

In Table 12-3 each of the criteria was equal to the quadratic mean of the incompatibility indicators:

Rating Criteria	Drumbane		Manorhamilton	Clara Hill		Killaloe	
	Grey	Rusty		Grey	Yellow	Buff	Grey-green
Chemical and mineralogical composition	7.1	3.5	0	0	0	5.8	6.5
Mass structure and pore space	10	3.5	5.8	8.7	5.8	6.5	6.5
Moisture transfer and breathing ability	0	0	5.8	0	0	0	0
Mechanical and thermal properties	3.5	7.1	7.9	8.7	7.1	5	5
Durability and appearance	3.5	3.5	0	3.5	3.5	7.1	7.1
Incompatibility Degree	5.9	4.2	5.1	5.7	4.4	5.5	5.7

Table 12-3: Incompatibility Degree calculated for the treatment of the samples and monuments

A brief comparison between these results suggests that the sandstone with which the consolidant treatments may be most compatible are the Drumbane Rusty and Clara Hill Yellow. Similarly the least compatible may be the Drumbane Grey, Clara Hill Grey and Killaloe samples. The results of both calculations are summarised in Table 12-4:

Criteria	Calculation by	
	Average	Quadratic mean
Chemical and mineralogical composition	3.4	4.4
Mass structure and pore space	6.3	7.0
Moisture transfer and breathing ability	0.5	2.2
Mechanical and thermal properties	5.3	6.6
Durability and appearance	2.9	4.6
Incompatibility Degree	3.4	5.3

Table 12-4: Summary of incompatibility criteria and ratings

The spread of the ratings show that the least compatible criteria are the mass structure and the mechanical and thermal properties. To the contrary the moisture transfer and breathing ability are of less concern when considering the treatment of these sandstones. As stated previously the main concerns regarding the mass structure include blocking of smaller pore sizes and the inability of TEOS to bridge larger gaps between particles.

These calculations include a certain amount of doubling-up in cases where the change in properties is known but the results or the analysis of combined effects is also included. This requires correction for the overlap between mass structure and moisture transfer criteria - for example, where fine pores or poor interconnectivity are highlighted as a risk to breathing ability but moisture transfer are actually seen to be lower. Therefore the distance between particles is the critical issue in regard to mass structure. This is out of the control of the conservator.

Consequently the more critical issue is the mechanical and thermal properties criteria. This rated highly because of the lower depths of penetration often achieved in all of the samples. Analysis showed that low penetration in the more susceptible samples greatly increased the risks to insolation stresses.

Although these calculations were only given as a rough guide, it has been shown that they can be a powerful tool in calculating the compatibility of treatments and the critical factors in each case.

Chapter 13:

Discussion

Guidelines on optimising success of consolidant treatments

13 Discussion: Guidelines on optimising success of consolidant treatments

The objectives laid out for this research focused on the durability of treated sandstone to continued weathering. The effectiveness of consolidant treatments in improving Irish sandstone's resistance to weathering has been presented throughout the results and analysis, and throughout the preceding discussion chapters. In the previous chapter, the compatibility of the consolidant treatments with the sandstones was evaluated. The following guidelines are suggested in order to optimise the likelihood of successful treatment:

13.1 Condition assessment and survey, history of surface conditions

Since the driving force behind any consolidant treatment ought to be the progress of weathering, this should be the first consideration. From the outset it is assumed that consolidant treatments are only being considered if there are visual signs that weathering is progressing towards an advanced state, or that the monument is at least slightly weathered but in a severely exposed environment.

It is of paramount importance that the environmental conditions that are causing the weathering are understood before treatment. If they are not addressed and actions taken to remove or reduce their effects then the long-term success of treatment is highly unlikely.

An assessment of the 'history' of conditions to which the stone surfaces have been subjected is also desirable. Relevant factors include the source of the stone, the effects of quarry sap, the construction and any changes to the construction of the monument and the evolution of the current exposure to moisture conditions, sun and wind. These are likely to indicate the mechanism of weathering present and what material has been lost as a result. A detailed photographic survey of the monument can be used to demonstrate differences in composition and weathering throughout the stone, as cementation and matrix minerals affect appearance and colour.

A detailed survey will also quantify the volumes, areas and depths of stone in each location, allowing the quantity of consolidants required to be estimated. It should be emphasised that simple quantitative methods can provide much useful information, as long as any assumptions and their limitations are subsequently highlighted.

13.2 Evaluation of stone properties and durability

The minimum level of information required prior to working out the suitability of a stone monument to consolidant treatment is an estimate of the range in values of open porosity. Estimates may be made on the moisture transfer and mechanical strength of the stone from the open porosity if the petrographic characteristics of the stone are known. If swelling clays are identified as constituents then greater detail is unavoidably required for this.

It would be preferable to have a rough estimate for at least one parameter each for mass structure, moisture transfer and mechanical strength. In some cases the only chance of doing so may involve selectively sacrificing one or two blocks to facilitate laboratory testing of a product and quantify the relevant properties. Attention should be paid to the quantities and accuracy of results prior to carrying this out.

The levels of damage that may be tolerable in doing so are case specific, although there are also many non-destructive techniques (NDT) available. To describe NDT further would be a step too far from this study's objectives, but many innovative solutions have been developed for a variety of applications. It is expected that NDT may provide information on the variability of properties and weathering in the stone for example, particularly on comparison with other available data. Non-critical trials may also serve to build knowledge of both the stone and treatment, particularly for awareness of the variability in properties. From this point of view it should be endeavoured to train conservators at consolidant application in a 'safe' environment prior to attempting to conserve monuments.

If suitably experienced persons are available then field trials on the monument itself may be a practical way to evaluate the performance of consolidant treatments in the exact conditions to which they will be exposed. There is no guarantee over what timeline any damage will occur however; there are obvious pros and cons to leaving trials for a long time before following up on treatment or abandoning the idea, with long-term trials effectively equating to leaving the monument to continue weathering indefinitely. Any measures of time-scale should be based on estimated rates of weathering in current conditions.

13.3 Choice of treatment

The most important objective in consolidant treatment is to choose a compatible one. This can be ensured by following the calculations of the Incompatibility Degree, and minimising the critical criteria as much as possible. To this end the results/output of the CI ratings may help to discriminate between the various factors and suggests which are most important, despite occasional overlaps. If all of the relevant factors are considered then the method is by definition unlikely to result in failure.

For example, in the previous chapter it was suggested from the CI ratings that the effects on breathing were less critical than the penetration of consolidants and the subsequent vulnerability of the treated surfaces to insolation stresses. Hence the addition of solvents will often be favourable, increasing the depths of penetration achieved. If the modulus of elasticity can also be better matched by the addition of nanoparticles this is also advisable, however excessive increases in modulus pose just as big a threat. The possibility of first applying TEOS or TEOS+solvent, followed by applications of low particle content PMC to optimise the treatment is a viable option. The sandstone acts somewhat like a filter, so the consolidants can continue to be absorbed after the particles are deposited, making a more successful treatment more likely.

Where necessary, a few scenarios should be analysed using the calculations for vulnerability to insolation stresses provided in *Chapter 11*. Simple assumptions on the range of depths of weathered material and of consolidant penetration can easily highlight the conditions with the greatest risks.

13.4 Specification of treatment

Once the treatment has been chosen and the critical parameters are highlighted, the specification must relate to the conservator not only the products and techniques but also the procedures appropriate to the anticipated range of characteristics and properties. The specification should include what assumptions are made in the choice of treatment, and direct persons how to record any problems if encountered. As mentioned earlier, the optimum action may vary according to porosity, cementation, weathering type, environmental conditions and availability of moisture. The proportion of additional solvent and nanoparticle contents appropriate for each of these should be stipulated.

13.5 Scheduling and control of applications

One way of taking control of the overall treatment may be to specify the application of consolidant treatments to only one or two small elements at a time, reducing the volume and area to be treated into more manageable sizes that are easy to keep track of. Each element and the applications made to it could be recorded using a checklist and a few simple measurements. Immediate scrutiny of the conditions could flag any necessary measures and quantify the appropriate levels of penetration or solvent required, for example.

Similarly it may be advisable to schedule long-term low resource rather than short-term high resource work programmes. This allows the conservator to develop skill and knowledge of both the stone and the treatments and can thus optimise the likelihood of successful treatment. There would also be more time to respond to developments and spot problems. With greater knowledge of the stone it may become apparent what the best treatment is, and works should be specified with this in mind.

Given the risks and the lack of experience in dealing with full-scale consolidant treatment more detailed recording of applications may be advisable. Recording of monuments is a basic requirement under the Venice Charter. Since large volumes of data are easily managed by IT systems it would be easy to indulge in data generation and processing of element specific information. Draft templates are provided in Appendix 13 to demonstrate the detail that may usefully be recorded. It is recommended that they be tailored to provide greater focus on the specific of each project.

Environmental management techniques can control or record the conditions prevalent during curing. This can be as simple as warning when relative humidity/temperature is approaching a defined limit. The data obtained during the treatment should be analysed to quantify the amount of consolidant applied. The level of consolidation can be calculated based on the amount applied and the expected quantities of by-products emitted. This may highlight if any locations/elements require a second treatment.

Consolidation of the typical TEOS products is between 90% and 95% complete within 2 to 7 weeks of application, depending on the product and on the environmental conditions. The process is effectively completed in a much shorter time period – within 2 to 4 weeks but may continue to gradually condense up to 60 days after application if a product of a lower degree of polymerisation is used.

Monitoring should take place after treatment to assess the progress of this. Monitoring also ought to look out for any deterioration in surface conditions or fracturing of the treated stone. If problems are spotted early subsequent applications can be adjusted or cancelled as necessary.

Chapter 14:

Efficiency in methodology for assessing the durability of sandstone and the effects of consolidant treatment

14 Efficiency in methodology for assessing the durability of sandstone and the effects of consolidant treatment

The efficiency of the methods used is addressed here using the accuracy and quality of the data obtained or by reference to some of the practical issues encountered.

14.1 Efficiency in methods for determining composition and structure of sandstone

14.1.1 Petrographic analysis

Inspection of the thin sections gave very useful characteristic qualities for each of the samples. It complemented the physical testing and helped to explain certain differences in both their properties and their weathering. The knowledge of the cements and pores was most useful in assessing the reasons for decay and the suitability of consolidant treatment.

14.1.2 SEM and EDX analysis

The SEM analysis did little for the characterisation of the sandstones or the treatments, although it did give some useful information on the stresses generated in the TEOS and PMC gels, and the effects of nanoparticle agglomeration in the latter.

The depths of penetration could not be evaluated using the SEM, due to sample size and the manner of preparation (cutting).

In this instance EDX analysis did not provide useful information on the composition of either the sandstone or PMC gel samples.

14.2 Efficiency in methods for determining physical properties of samples

The methods used to determine the physical properties of the samples (*Section 5.2.2*) were quite laborious, as the majority of work was based on gravimetric measurements. A high number of readings taken at regular intervals were required, from which all of the properties were then calculated.

14.2.1 Mass structure

The mass structure was determined using the methods based on Archimedes' principle. The size of the vacuum bowl determined the number of samples that could be tested at once, thus determining the scheduling of the test programme. There were no problems establishing a sufficient vacuum before putting in the water. The accuracy of the balance was ±0.1g.

The porosity was a useful and simple property by which to classify the samples relative to each other. It was easily related to the moisture transfer and mechanical strength properties, and was also notable in regard to both weathering and treatment.

14.2.2 Moisture transfer

The readings required for the moisture transfer properties were most demanding because of the number of samples involved and the timing intervals involved.

It was sometimes necessary to determine the values for capillary absorption and evaporation in planes both parallel and perpendicular to the samples' bedding to ensure that the required values were obtained. This was due to the differences in the weathering of samples. This added a significant amount of high quality but somewhat redundant data. The results were quite similar in most of the samples, albeit for several of the Drumbane Rusty and Manorhamilton ones which had notably anisotropic structures.

14.2.3 Mechanical strength

The number of cubes of samples that were suitable for crushing was sometimes not sufficient to determine the mechanical strength accurately. Due to the objectives of the research the durability was considered to be of paramount importance therefore the samples were weathered. However, after having been subjected to weathering, many of the cubes were not suitable for crushing because of uneven surfaces.

The use of the Schmidt hammer rebound test was compromised because certain samples fractured on impact due to brittleness or planar discontinuities. Once the faces had been weathered the hammer became less and less 'non-destructive.'

The use of the PUNDIT ultrasonic velocity meter was inappropriate before treatment, as the grease required to ensure correct measurement could not be guaranteed to be removed, and this could have affected the results obtained for consolidant treatment.

14.3 Efficiency of methods for causing decay and determining weathering resistance in sandstone

The laboratory conditions were specifically tailored to be less conflicting with field conditions. For example, by weathering the samples in advance of consolidant application, they were quite similar in condition to decaying monumental surfaces. They were more comparable because the variations in surface roughness were more representative and pore structure was altered accordingly.

The occurrence of fracturing as a form of decay is more characteristic of artificial weathering than of normal environmental weathering, as already discussed in *Sections 8.1* and *3.1.5*. Fracturing helped to increase capillary absorption in samples due to the larger open voids through which moisture could flow. Hence if anything capillary absorption was perhaps higher than it might be in monuments, so the presented analysis of moisture transfer may be slightly more unforgiving.

The results for the percentage mass lost due to artificial weathering cycles were easily used to classify the sample's durability relative to each other. Their performance could then be reasoned in regard to individual sample composition and properties.

As described in RILEM (1980), Test No. V.2, partial immersion tests are not as suitable for determining mass losses; however as presented in *Section 6.2* the combined effects of weathering and washing also allowed for a reasonable comparison of the properties both before and after.

14.4 Efficiency of methods for determining the success of consolidant treatment

All surfaces were laid horizontal during consolidant application so that runoff was minimised. As a result the absorption and penetration may have been slightly different to monumental conditions as the treatment was more likely to penetrate downwards.

14.4.1 Comparison of unweathered, weathered and treated sample durability

The results for the durability tests seemed to be more informative than the results for the depth of penetration tests. The effects of the weathering were much more demonstrative of the sample's composition and physical properties, as discussed above. Overall the method did achieve its objectives and gave greater information than a straight-forward comparison of treated and untreated samples subjected to accelerated weathering, as is commonly carried out.

14.4.2 Depth of penetration of treatments

The success of the penetration was quite difficult to verify using the Water drop absorption test. Some of the results were statistically poor. This was mainly due to arbitrary numerical calculations and poor repeatability, resulting in both good and bad results. The depths of penetration determined from the Water drop absorption test were generally very low (5-12mm) in comparison with the previously recommended value of 25mm. Only the Manorhamilton sample was observed to have a sufficient value according to these previous recommendations (maximum 30mm).

Visual observations made during the Surface wetting test identified drying and wetting phenomena that were most useful for determining the depth of penetration. The method was repeatable and gave greater insight on the effects of weathering and penetration on the inner structure of the cubes. The readings obtained for depth of penetration with the Surface wetting method were moderately higher (majority 9-13mm), but still relatively low.

Estimation of depth of penetration by weathering cross sections was a direct and insightful method to assess the success of penetration, but only in certain samples. Occasionally the observed decay effects also showed up the absorption profile of the consolidant.

Other methods used to determine the depth of penetration such as staining with dithizone and ultrasonic tracing were not favoured. The former was deemed (by others) inappropriate due to the iron content in most of the samples. The latter was not favoured as the cross sections were quite variable due to both composition and the effects of weathering and treatment.

The depth of penetration was not an easily derived value. It had high deviation and was occasionally poorly related to either composition or physical properties. It was a poor measure to use as a determinant factor in assessing the effectiveness of consolidation.

The results were most useful in assessing the risks of insolation stresses, as discussed in *Chapters 11* and *12*.

The information provided gives an overall picture of the penetration achieved when complementary methods are considered in tandem.

Chapter 15:

Conclusions and further work

15 Conclusions and further work

The sandstone samples were characterised, weathered and treated in the laboratory to simulate the condition of the monuments, understand the weathering mechanisms and the effects of applying modified and unmodified TEOS consolidants to protect them.

Analysis was based on sample composition and properties; mineral content, pore characteristics, mass and mass structure, moisture transfer, mechanical strength, the effects of weathering and the appearance of decay.

15.1 Characterisation of Irish sandstone

The characterisation of the samples has provided much information on the variability of properties with composition, and the influence of pore characteristics in particular:

- Drumbane sandstone is of medium to high density, and medium to low porosity, depending on its grain size, packing and iron and matrix content. Drumbane sandstone has medium capillary absorption and evaporation. Where grey in colour it is of high strength, modulus of elasticity and surface hardness. Where rusty in colour, it is of low-medium strength, elasticity and surface hardness.
- Manorhamilton sandstone is medium in density, and is of medium to high porosity, depending on matrix content. Manorhamilton sandstone has medium-high capillary absorption and evaporation. It is of medium-high strength, elasticity and surface hardness.
- Clara Hill sandstone has medium to low density and low to high porosity, depending on cement content, grain size and sorting. It has low strength and modulus. Where grey it has medium density and capillary absorption but low evaporation due to poorer interconnectivity of the pores. Where yellow it is of low density, has high moisture transfer properties and its strength and modulus are even lower due to poor cementation and matrix content.
- Killaloe sandstone generally has high density, low porosity, low capillary absorption and low evaporation, with the exception of the Dark Grey type which is highly variable. It is of high strength, elasticity and surface hardness.

15.2 Weathering of Irish sandstone

15.2.1 Decay types

Decay effects similar to those observed in the monuments were recreated. Fracturing occurred often due to the weathering mechanisms of salt crystallisation in finer pores in low and medium porosity samples. The highest losses occurred in samples of medium to high porosity containing high iron and clay contents, involving granular disintegration and differential erosion. The differences between granular disintegration and flaking were attributed to the strength and extent of cohesive constituents. Flaking involved greater increases in evaporation than the other types.

15.2.2 Effect of weathering on samples' properties

The weathering effects increased porosity by 15-30%, except where differential erosion occurred. Increases were higher where fracturing was present.

The capillary absorption coefficient was increased by approximately |0.95*Porosity| $g/m^2/s^{1/2}$, while long-term rates were reduced. Evaporation was increased by approximately |1.1*Porosity| $g/m^2/hr$, but affected high porosity samples more in the long-term.

Mechanical strength was reduced by between 15% and 80% in samples of high porosity and low cement and matrix content, due to the loss of cohesion caused by weathering. Samples having high strength were considerably less affected.

15.2.3 Comparison of artificial weathering and the weathering observed in the monuments

The differential erosion and granular disintegration in the west doorway and façade of Cormac's Chapel were recreated in the laboratory with the Drumbane samples. Long term high moisture content has caused the flaking observed on the east side, which was recreated to a small extent in the samples. The fine matrix content provides greater cohesion and protects the surface from the erosion seen in the west façade.

The weathering of both silica and silicate minerals in the doorway of St. Brendan's Cathedral was initiated by long-term diffusion processes facilitated by high moisture content. Salt crystallisation is now the greatest contributor to decay. The variability of colour was seen in both the unweathered and weathered samples of Killaloe sandstone. It is very durable so granular disintegration was barely seen in the samples tested in the laboratory.

15.3 Consolidant treatment of Irish sandstone

15.3.1 Application of consolidants modified with solvents and nanoparticles

Differences in the composition of commercial TEOS products affect the progress of gelation and the generation of stresses within the gel. Modification of the consolidants allows control over the application, tailoring to specific requirements and offering more compatible choices. Consolidant should be brushed on until absorption is complete. The manufacturer's instructions should be followed and good time allowed so that each element is treated properly.

Consolidants with lower viscosity and surface tension achieve better penetration into sandstone. Adding solvent content to the consolidant treatment further aids penetration. Low viscosity ketone solvents are best added to treatments for sandstones of lower porosity, pore interconnectivity or moisture transfer properties. They also reduce the mass of consolidant deposited, depending on pore characteristics and the consolidants' liquid properties.

Nanoparticles are best added to treatments for sandstones of higher porosity or if the cohesion between particles is especially poor. Particle Modified Consolidants (PMC's) have significantly improved modulus properties and provide greater resistance to stresses.

High content PMC's are less suitable due to agglomeration of the nanoparticles subsequently altering appearance and blocking pores. Nanoparticle sizes and contents should be chosen carefully to avoid agglomeration. The ones used were too small and mutually aggregated. PMC's should contain =10% nanoparticles by volume and be adequately dispersed in Isopropanol solvent using ultrasonic mixing before addition to the consolidant. Inappropriate use of PMC's was shown to reduce the likelihood of treatment success.

Some samples were noticeably darker where comparing treated and untreated parts. Agglomerated nanoparticles may gather leaving whitish marks on rough surfaces.

15.3.2Effects of consolidant treatment on physical properties

For samples of 10% porosity, an increase in mass of less than 1% or 850 g/m^2 should be expected. The porosity of sandstone should be reduced by <10% due to treatment, except where PMC's are applied. High content PMC's decrease porosity by =4 times more than other treatments do.

Capillary absorption coefficients should be reduced by between approximately 5 and 10 g/m^2/$s^{\frac{1}{2}}$, depending on porosity and pore characteristics (correlation = 0.25*OP g/m^2/$s^{\frac{1}{2}}$, OP in %). This is accompanied by a shift in the progress of absorption. Rates of evaporation were decreased by up to 7.5 g/m^2/hr in low porosity samples. The evaporation in higher porosity samples was relatively unchanged.

Consolidant treatment generally increased the samples' compressive strength and modulus of elasticity, although the data obtained was not good enough to suggest a wider trend.

15.3.3Effects of consolidant treatment on improving cohesion and durability

Treated samples lost several times less material than weathered/untreated samples, showing that TEOS-based consolidants provide significant resistance to weathering mechanisms. Sandstone can be more brittle after both weathering and consolidant treatment due to changes to cementing actions, the loss of fine matrix accommodating strain and the presence of local variations due to consolidant treatment. Where porosity is high and matrix materials are absent consolidant bonding does improve cohesion between the constituents but is open to erosion by further weathering. PMC treatments may be more suitable for such conditions.

Visual comparisons demonstrate that further weathering can have a greater impact on the appearance of the stone despite less material being removed.

15.3.4 Effects of weathering and treatment on sandstone's breathing ability

The changes discussed in *Chapter 10* suggest that treatment, although being slightly restrictive to sandstone's breathing ability, reduces the absorption characteristics such that treatment is beneficial. The evaporation of moisture is reduced, but the levels of moisture absorbed into the stone ought to be reduced by a greater amount. This is because of the net changes in mass structure and moisture transfer properties caused by treatment.

15.3.5 Effects of consolidant treatment on insolation stresses

The higher modulus of elasticity in treated sandstone to the depth of penetration increases thermal differential stresses. The model of Hosek & Panek (1985) showed that tensile stresses may be almost doubled in sandstone as a result. Cyclic insolation stresses are assumed to reduce the tensile strength due to fatigue, although these effects are greater if other weathering mechanisms occur simultaneously. The samples identified to be most at risk fractured when subjected to the artificial weathering.

15.4 Effectiveness and compatibility of monuments for consolidant treatment

Individual analysis of the samples' characteristics and properties revealed that most are suitable for treatment. A comparison of the durability of treated and untreated samples to further weathering showed that treatment offers considerable protection:

- Drumbane sandstone is suitable for consolidant treatment, as the effects of weathering were reduced considerably by treatment. Treatment of the east doorway of Cormac's Chapel is not as likely to be as successful as for the west doorway due to moisture and biological growth, and the inability of TEOS to bridge gaps in flaky blistered material. Nanoparticle additions may help to overcome this. The risks of fracturing and insolation stresses are highest in the Rusty type so adequate penetration must be ensured. Any PMC application should be carefully controlled so as to avoid increasing the risks of insolation stresses.

- Manorhamilton sandstone is suitable for consolidation, as the effects of weathering were reduced considerably by treatment. Treatment should preferably be with PMC treatments because of low matrix constituents. Its percentage saturation is not greatly affected by either weathering or treatment because of the high interconnectivity of the pores.
- The variations in the Clara Hill samples resulted in different responses to treatment. Some Grey samples had poor interconnectivity and continued to fracture badly even after treatment. Treatment is less suitable for them because of the greater risk of damage due to insolation stresses combined with lower mechanical strength. The comparative weathering rates between treated and untreated samples show consolidation to be effective nonetheless.
- The Clara Hill Yellow sandstone is more suitable for treatment than the Grey type as the risks of poor penetration and insolation stresses are determined to be slightly lower. The high interconnectivity of the pores continues to allow the stone to breathe and endure better than if left untreated.
- The Killaloe samples were successfully treated achieving appreciable depths of penetration despite low porosity and fine pore sizes. Further weathering did little to test the durability of the treated stone and it was less representative of the weathering in the sandstone at St Brendan's Cathedral. The weathered stone requires consolidant treatment to reduce the effects of continued weathering, possibly using low nanoparticle content PMC treatments to ensure adequate bridging between particles where cohesion has been reduced.

15.5 Efficiency in the methods used for assessing consolidant effectiveness

The physical properties measured provided sufficient data to ascertain the effects of weathered and treatment processes of the samples and relate them to the condition of the monuments.

Consolidant effectiveness was best determined by comparison of untreated and treated samples' weathering. Complementary techniques including methods of observation were best for determining the depth of penetration.

15.6 Recommendations to conservation professionals

To obtain the best information and carry out successful treatment of sandstone with consolidants it is necessary to understand both the surface and environmental conditions of the monument. This may be achieved by carrying out several tasks one after the other, bearing a few guiding principles in mind:

- Sandstone composition and properties are interdependent and affect appearance
- Variations in appearance of stone may reflect changes in either its composition or its resistance to exposure
- Key mechanism of consolidant action is by lining pores and forming bonds between adjacent grains where gaps are not excessively large
- Key susceptibilities of consolidated stone are breathing and subsurface stresses

The development of the craftsperson's experience in dealing with the stone material and in making intuitive calculations must be encouraged. They should be equipped with a document containing protocol for them to make tailored calculations based on local variations in the stone, according to their experience. This should contain minimum and maximum criteria for the addition of solvent and nanoparticle contents.

15.6.1 Calculations of relevant in-situ properties and factors during application

To take control of the consolidant treatment process it is best to proceed one stone at a time if possible. Considering the volume, porosity and absorption values of each element individually allows simple step-wise calculations of the volume of consolidant and duration of application required. It also facilitates monitoring of the progress of the treatment and better documentation of the application should be possible. If any problems do arise afterwards the reasons for them can be assessed by comparison with other elements.

15.7 Further work

Field trials and monitoring may be used to assess the consolidants on the monuments themselves, where appropriate. In-situ tests may also provide information on the actual values for physical properties, in case correlation or extrapolation is needed compared to those measured in the laboratory.

The data presented is sufficient to model the movement of moisture in sandstone and the interaction of constituents with decay processes. This could provide information on the continued weathering or structural stability and be used to develop maintenance plans for the monuments.

The addition of the capillary absorption rates over specified time periods allows for further comparison between the samples than if the capillary absorption coefficients alone were presented. This may also prove useful when monitoring the absorption of consolidants during application.

The optimisation or design of PMC treatments for application to sandstone monuments would be most useful, indicating the solvents and nanoparticle sizes most suitable for sandstone according to porosity, absorption or decay characteristics.

References

16 References

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Appendix 5:

Measurements and calculations

Appendix 5: Measurements and calculations

This Appendix comprises examples and illustrations of all of the measurements made during the laboratory testing. Subscript references - U unweathered, W weathered, T treated.

<u>General properties:</u>

- Dimensional measurements

Numbering of edges (12 no.) of each cube using Vernier callipers to ±0.1mm:

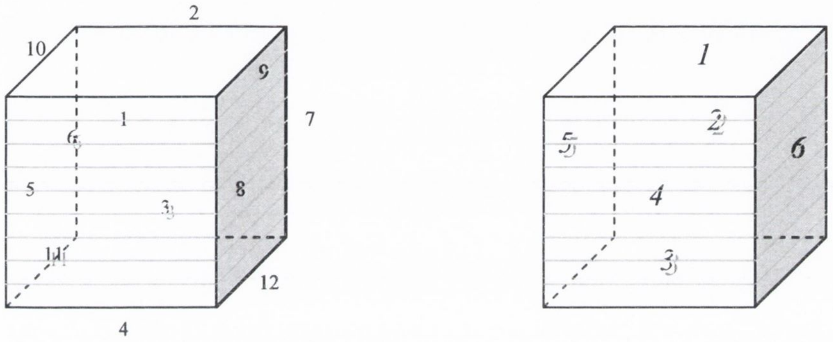

Figure A5-1: Numbering of cube edges and faces for measurements

- Gravimetric measurements (all to ±0.1g)

Dry mass after drying in oven for 24 hours and cooling to room temperature m_d

Saturated mass after 24 hours immersion in water introduced in a vacuum, free surface moisture removed by patting with a damp cloth m_s

Bouyant mass after 24 hours immersion in water introduced in a vacuum m_h

- Calculation of mass structure properties:

[1] Apparent density (kg/m^3)

$$\rho_b = m_d/(m_s - m_h)*\rho_w ,$$

$$\text{where } \rho_w = 1000 \text{ kg/m}^3$$

[2] Open porosity (%)

$$p_o = (m_s - m_d)/(m_s - m_h)*100$$

- Calculation of moisture transfer properties:

Mass at time intervals m_i during evaporation and capillary absorption, Gravimetric measurements (all to ±0.01g)

[3] Percentage saturation (%)

$$S = (m_w / \rho_w) / v_p * 100$$

[4] Evaporation rate ($g/m^2/hr$)

$$q(t) = M / t$$

[5] Capillary absorption coefficient ($g/m^2/s^{1/2}$)

$$C_{exp}(t) = M / t^{1/2}$$

where $M = m_w / A$, and $m_w = m_o - m_i$

where $m_w = m_o - m_i$, and A is the area calculated using the relevant dimensions of the face/plane through which moisture transfer is occurring.

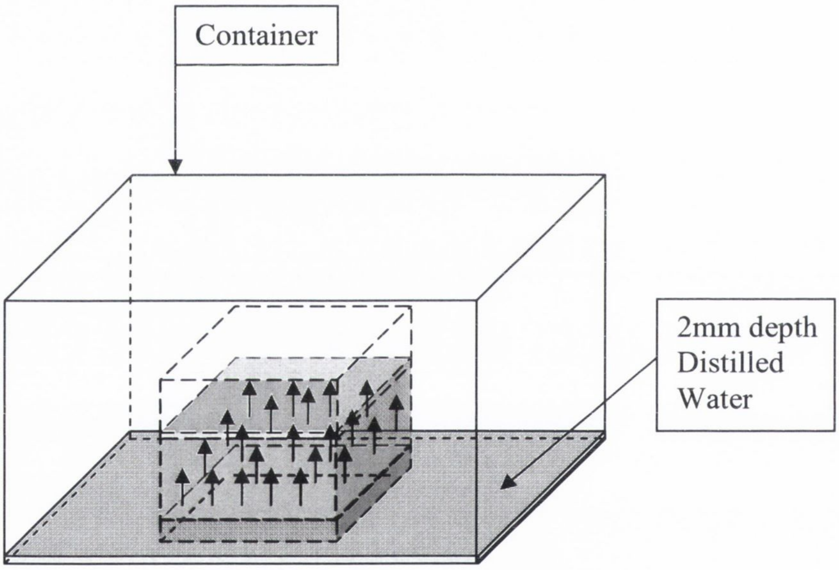

Figure A5-2: Capillary absorption of moisture during tests for moisture transfer properties

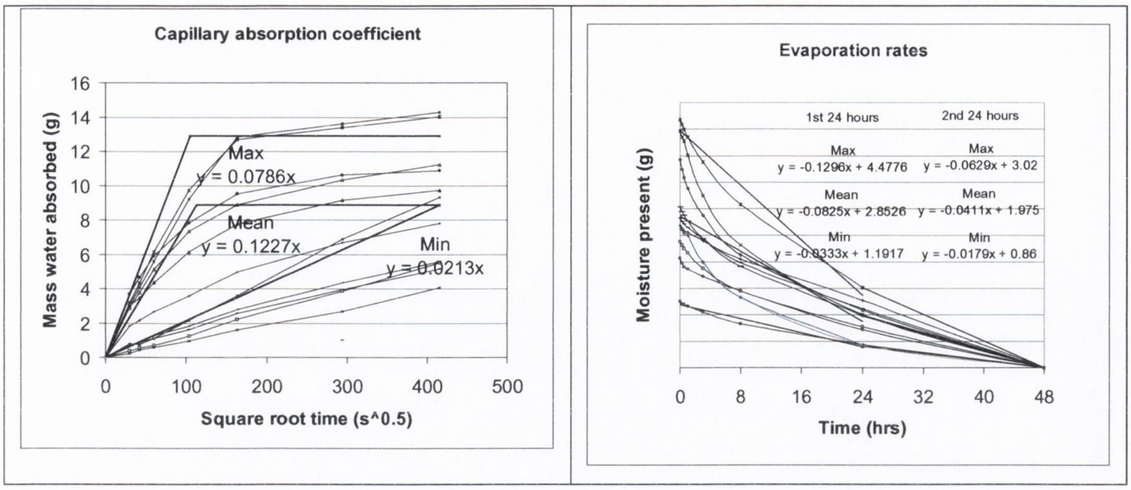

Figure A5-3: Calculation of moisture transfer properties

- Measurements taken for mechanical strength properties:

Stress and strain using load cell (*P*), strain gauges (*e*) and workstation
Time *s* taken for ultrasonic pulse through cube of thickness *t* using PUNDIT apparatus
Surface hardness values (read directly off calibration chart of Schmidt hammer)

- Calculation of mechanical strength properties:

[6] Compressive strength (N/mm^2)

$$s_{max} = P_{max}/A$$

[7] Modulus of elasticity (crushing) (GPa)

$$E = s/e$$

[8] Modulus of elasticity (PUNDIT) (GPa)

$$E = V^2 . \rho$$

where, $V = t / s$

- Measurements taken during weathering:

Samples considered weathered after 15 cycles of weathering and 80/120 cycles of washing
Mass structure, moisture transfer and mechanical strength properties as before

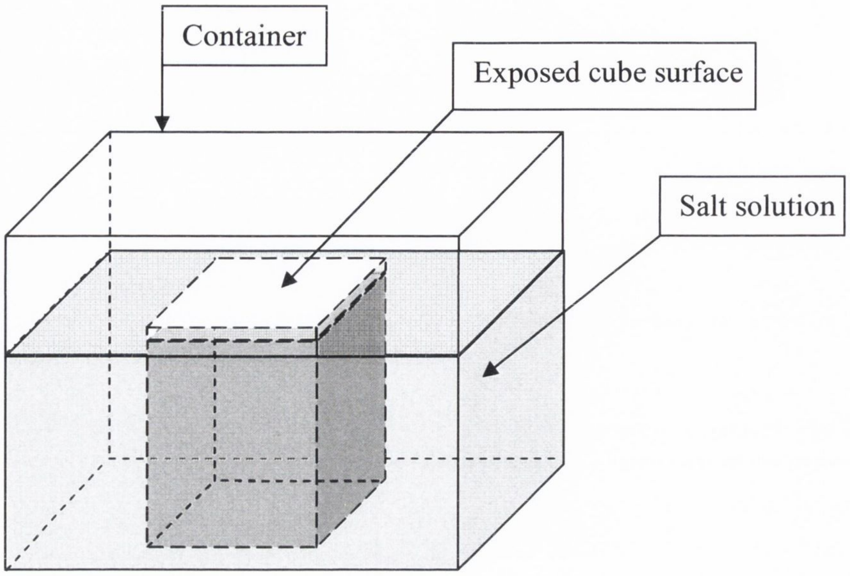

Figure A5-4: Arrangement of samples subject to partial immersion in salt solutions

Gravimetric measurements of cubes (±0.01g)
Dry mass at room temperature following x cycles of immersion in salt solution for 3 hours and drying in oven for 21 hours m_x
Dry mass at room temperature following n cycles of drying following washing m_n
Ionic conductivity using handheld conductivity meter:
Conductivity of solution (±1000μS/cm – high salt concentrations)
Washing (±5μS/cm – low salt concentrations / ±100μS/cm – high salt concentrations)

- Calculations for weathered samples:

Mass of material lost (g)
[9] $m_u - m_w$
Integration of exponential plot of estimated salt concentrations after n cycles of washing
[10] $\int_0^N [S_{max}]e^{-n}.dn$

- Measurements taken during consolidant treatment:

Gravimetric and volumetric measurements of consolidant products, solvents and nanoparticles
Time for known volume of liquid to flow through capillary = $t_1 - t_2$
Gravimetric measurements of cubes during application of consolidants - measured when fully surface saturated m_t
Time s for known volume of liquid V to flow through thin capillary tube at atmospheric temperature and pressure

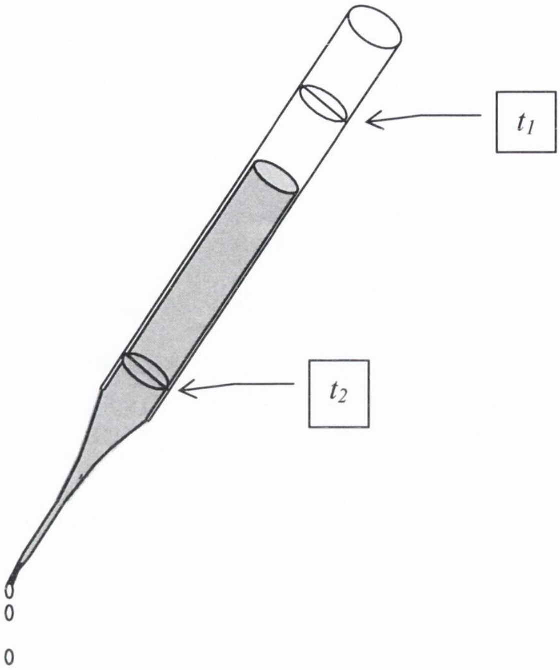

Figure A5-5: Measurements taken for estimating liquid viscosities

- Calculations for amount of consolidant applied

[11] Comparison with time taken for liquid of known viscosity

$$\mu_{\text{liquid}} = (t_1 - t_2)_{\text{liquid}} / (t_1 - t_2)_{\text{water}} * \mu_{\text{water}}$$

[11] Percentage of products evaporated during curing (%)

$$(m_t - m_d) / m_d$$

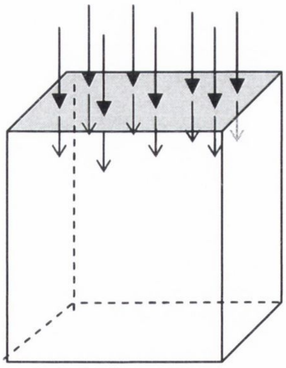

Figure A5-6: Application of consolidant treatments to samples

- Measurements taken on consolidated samples:

Mass structure, moisture transfer and mechanical strength properties as before
Time *s* for absorption of water droplets at distance *d* from application surface
Depths to which consolidants were visible
Depths at which wetting/drying effects observed

- Calculations for consolidated samples

[12] Gain in mass (g)

$$m_t - m_w$$

[13] Depth of penetration (mm)

$$d(s > s\ average)$$

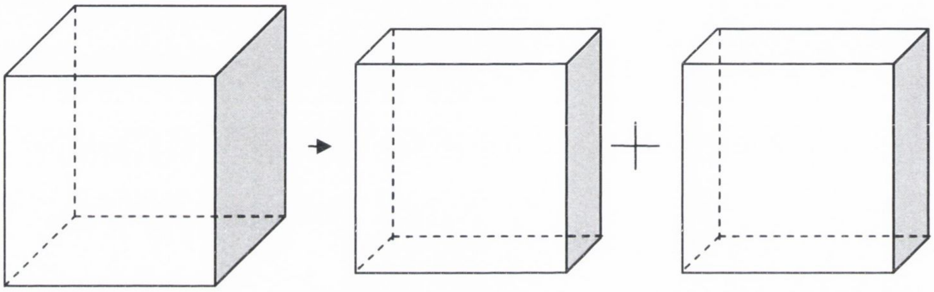

Figure A5-7: Cutting of samples to determine depth of penetration

- Measurements taken on samples after further weathering:

Mass structure and moisture transfer properties as before
Depths to which consolidants/weathering were visible
Dry mass at room temperature following *x* cycles of immersion in salt solution for 3 hours and drying in oven for 21 hours m_x
Ionic conductivity using handheld conductivity meter

- Calculations for samples after further weathering:

[14] Mass of material lost (g)

$$m_t - m_{w2}$$

[15] Depth of penetration (mm)

$$d(\Delta m < \Delta m\ average)$$

Appendix 10:

Saturation profiles of samples

Appendix 10: Saturation profiles of samples

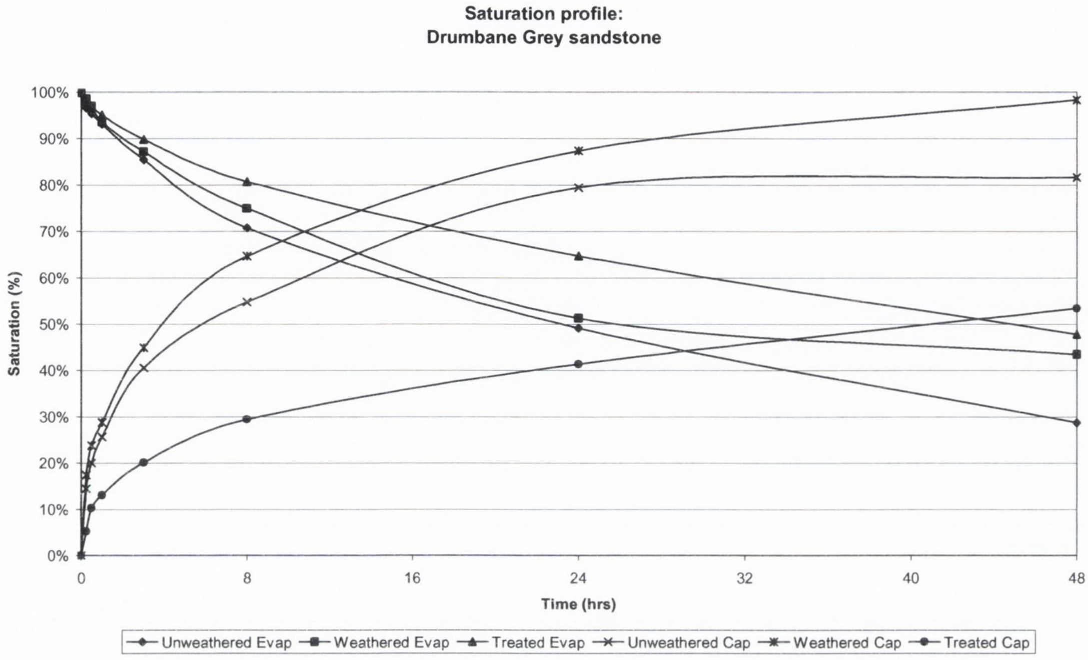

Figure A0-1a: Comparison of saturation profile of treated Drumbane Grey samples during capillary absorption and evaporation with unweathered and weathered profiles

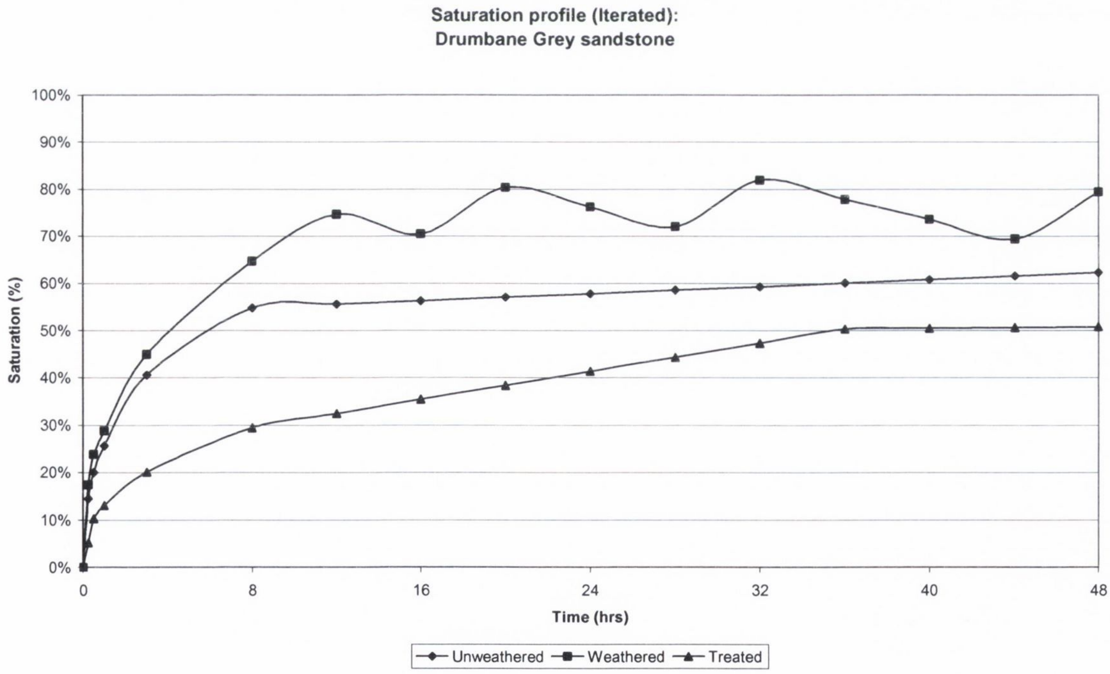

Figure A10-1b: Composed saturation profiles of unweathered, weathered and treated Drumbane Grey samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

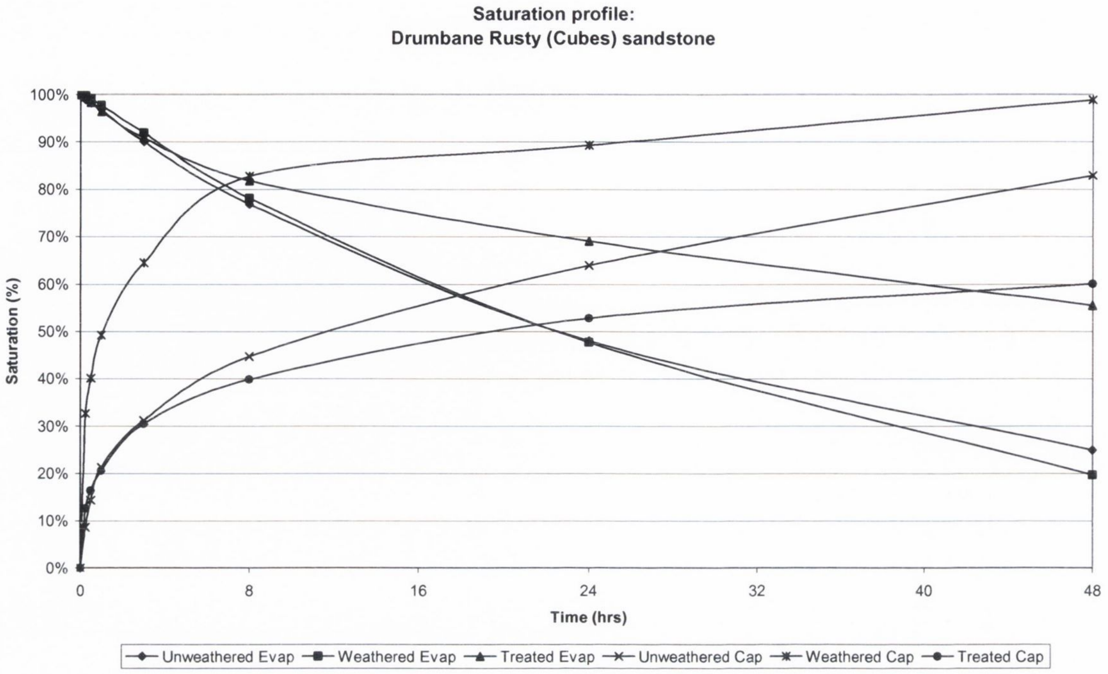

Figure A10-2a: Comparison of saturation profile of treated Drumbane Rusty (Cubes) samples during capillary absorption and evaporation with unweathered and weathered profiles

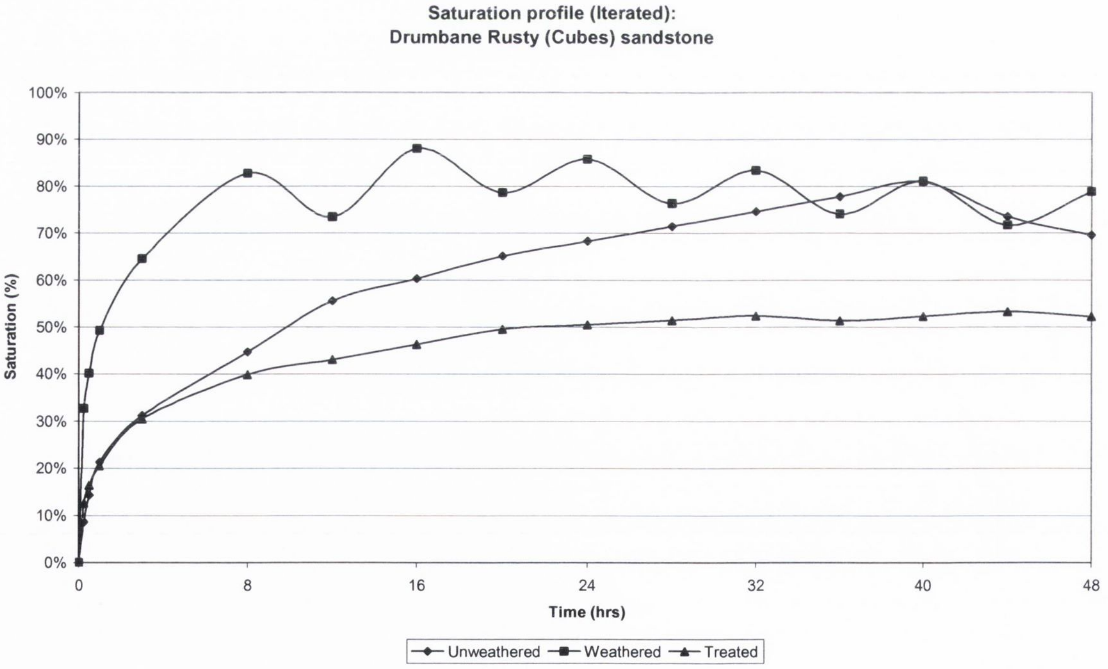

Figure A10-2b: Composed saturation profiles of unweathered, weathered and treated Drumbane Rusty (Cubes) samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

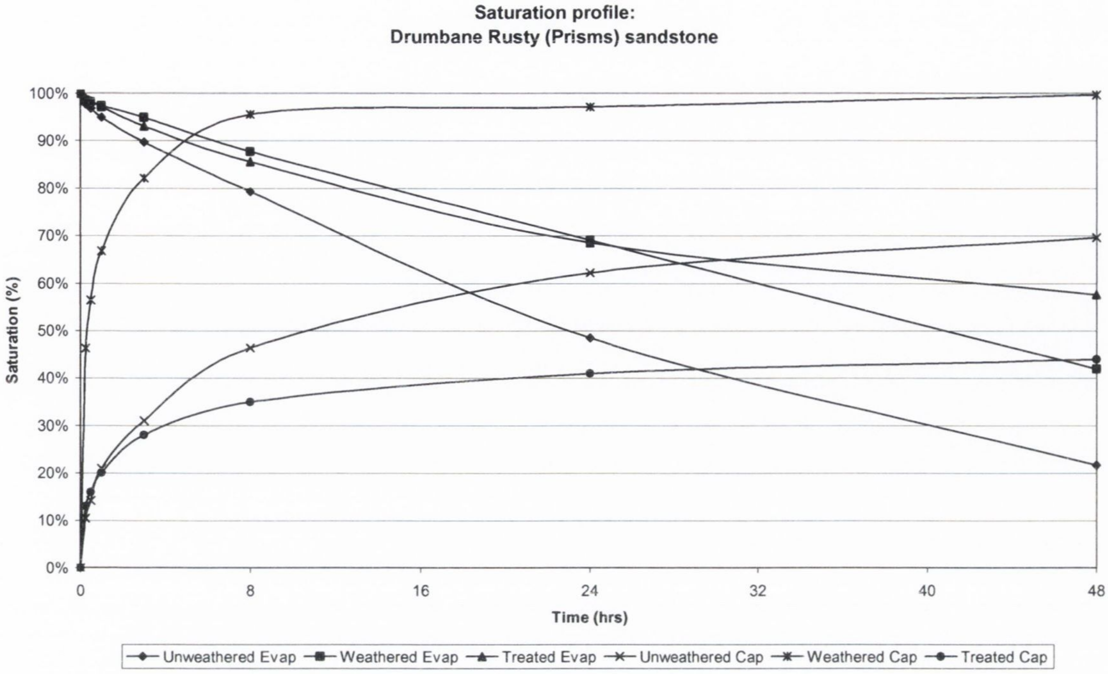

Figure A10-3a: Comparison of saturation profile of treated Drumbane Rusty (Prisms) samples during capillary absorption and evaporation with unweathered and weathered profiles

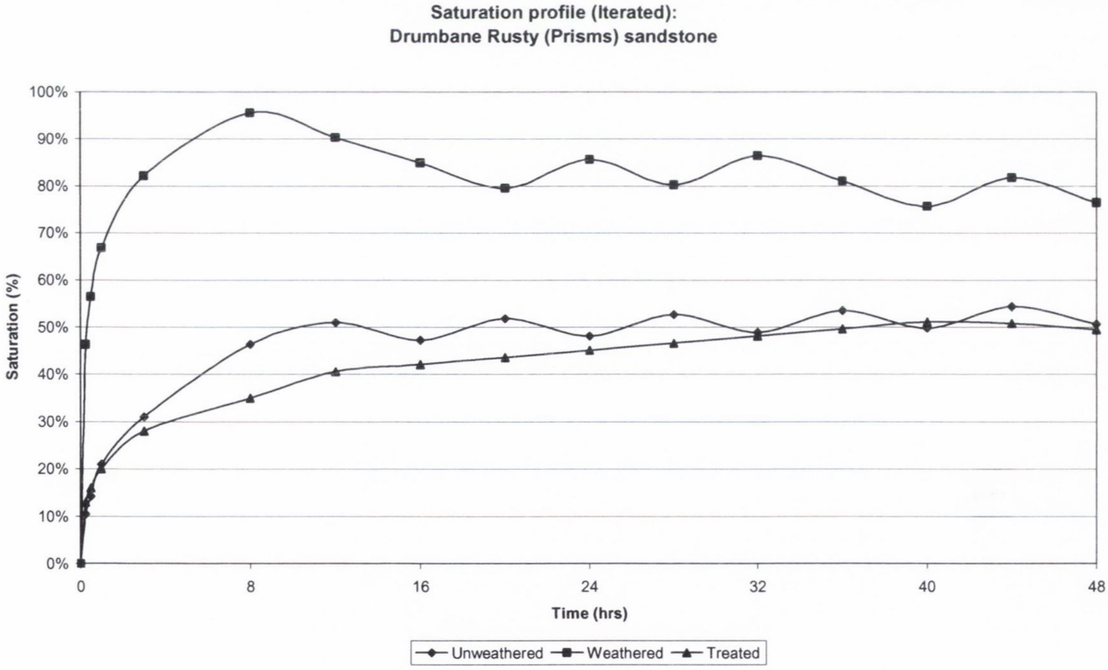

Figure A10-3b: Composed saturation profiles of unweathered, weathered and treated Drumbane Rusty (Prisms) samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

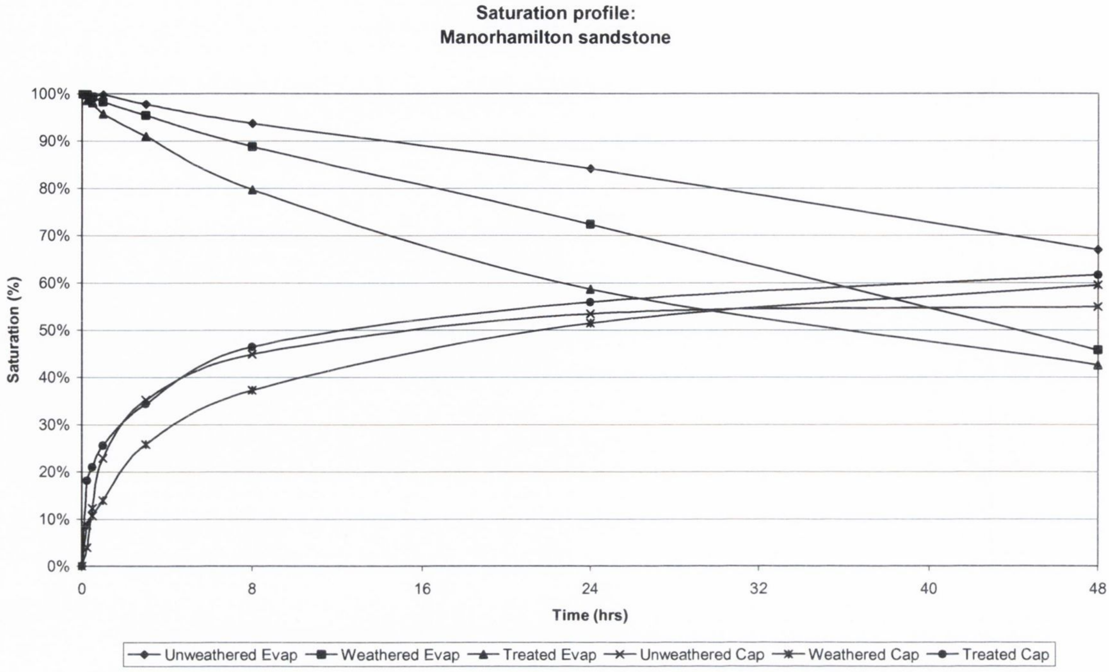

Figure A10-4a: Comparison of saturation profile of treated Manorhamilton samples during capillary absorption and evaporation with unweathered and weathered profiles

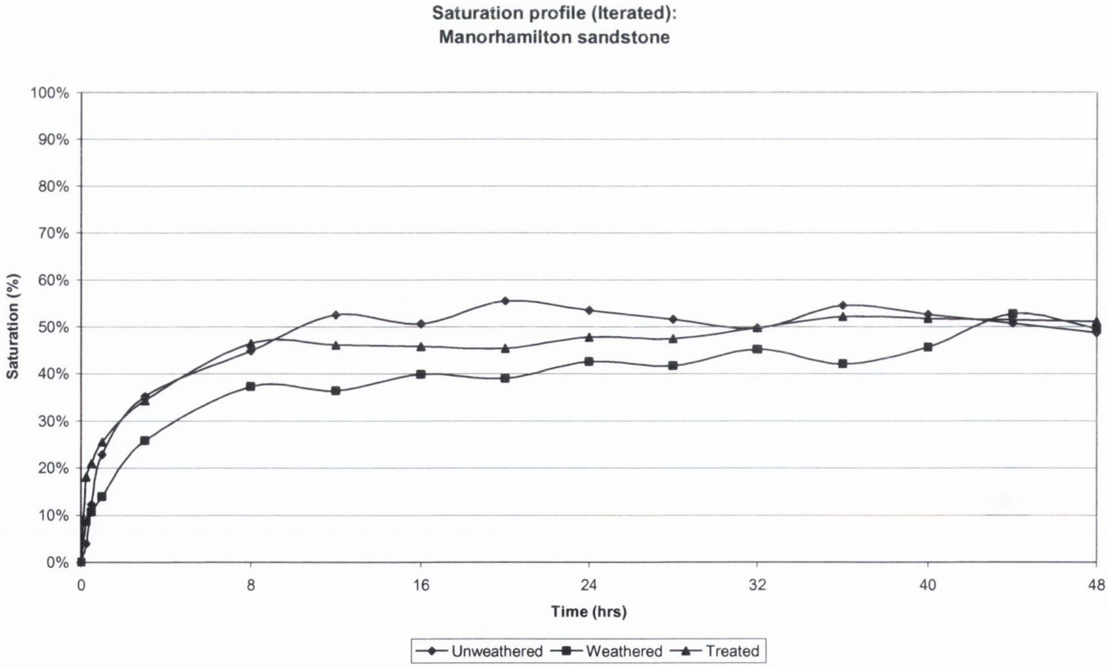

Figure A10-4b: Composed saturation profiles of unweathered, weathered and treated Manorhamilton samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

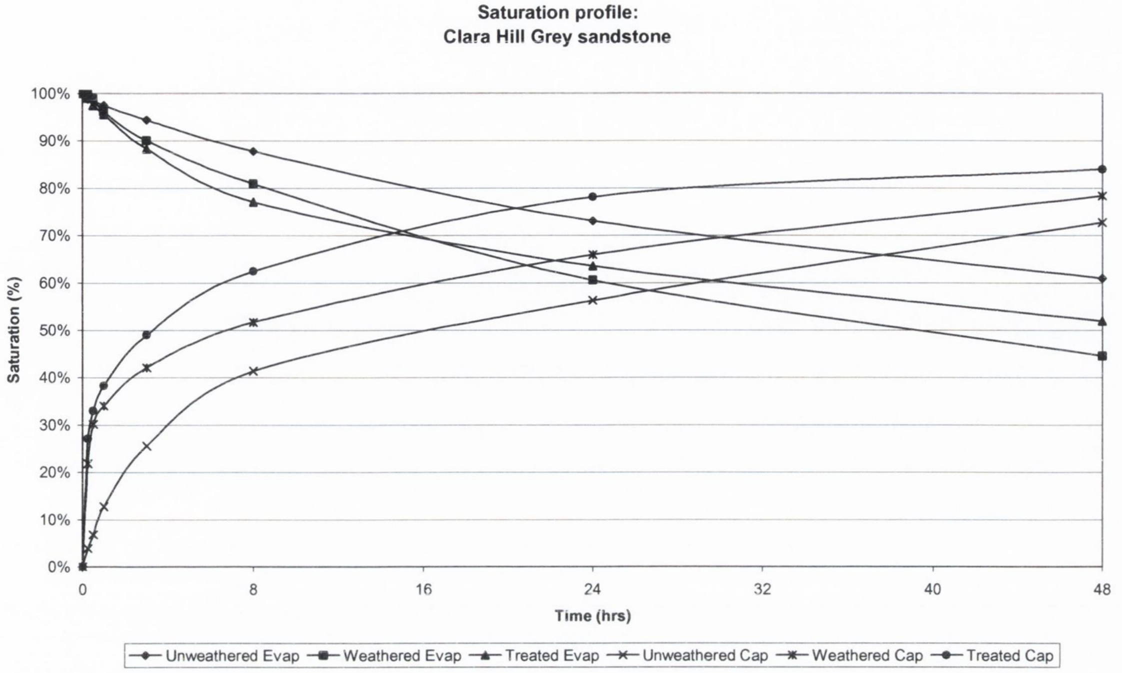

Figure A10-5a: Comparison of saturation profile of treated Clara Hill Grey samples during capillary absorption and evaporation with unweathered and weathered profiles

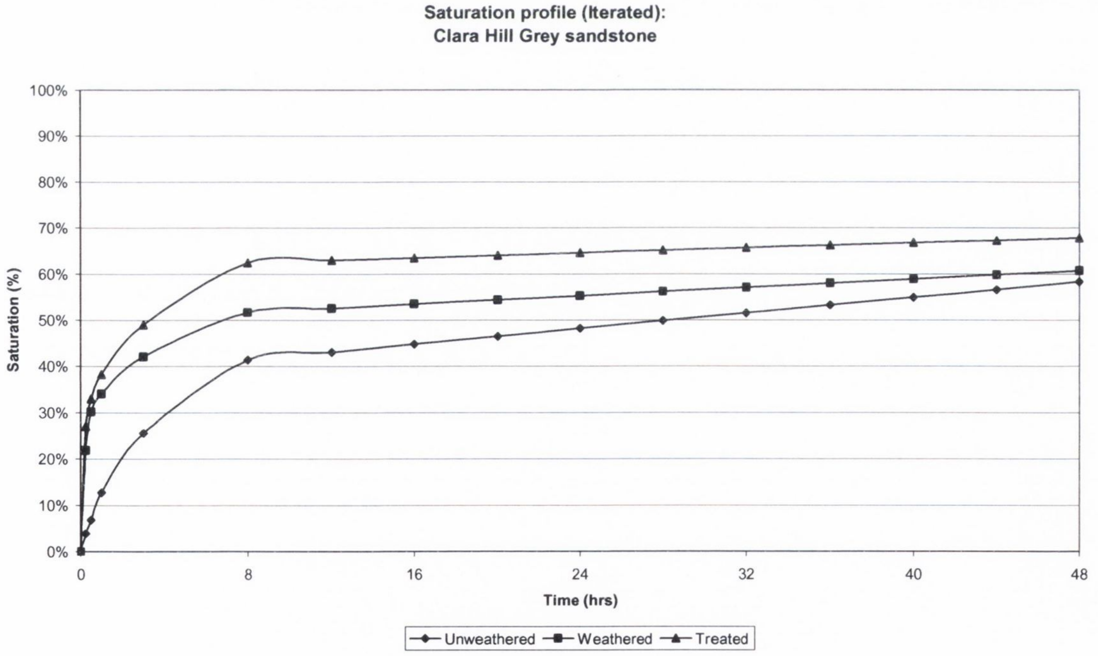

Figure A10-5b: Composed saturation profiles of unweathered, weathered and treated Clara Hill Grey samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

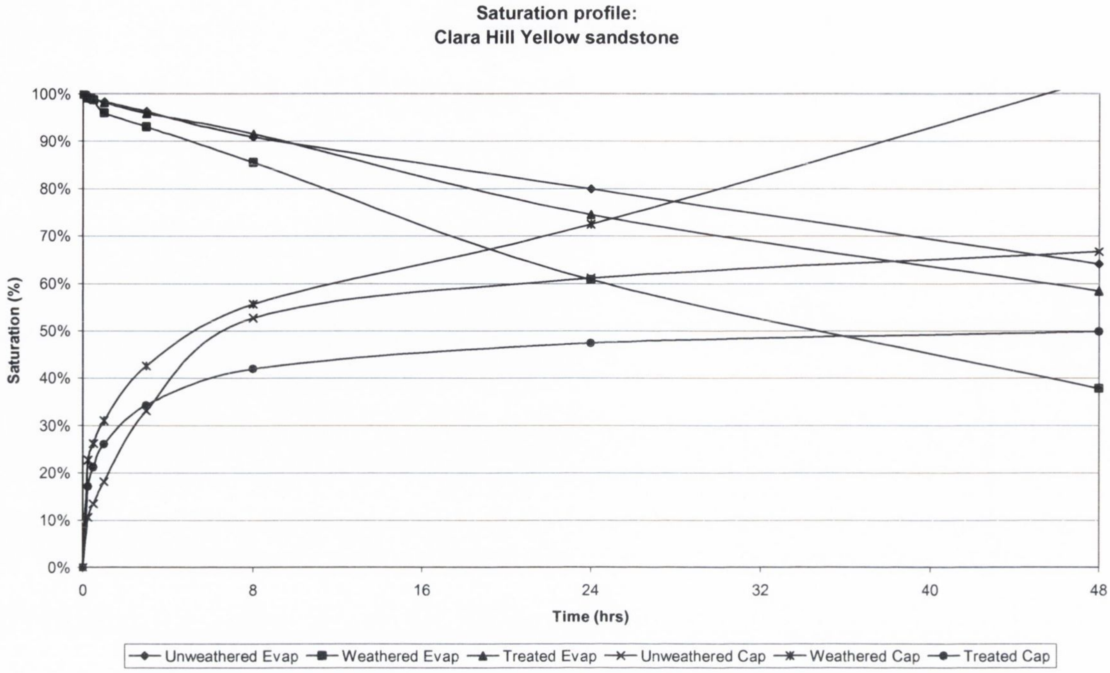

Figure A10-6a: Comparison of saturation profile of treated Clara Hill Yellow samples during capillary absorption and evaporation with unweathered and weathered profiles

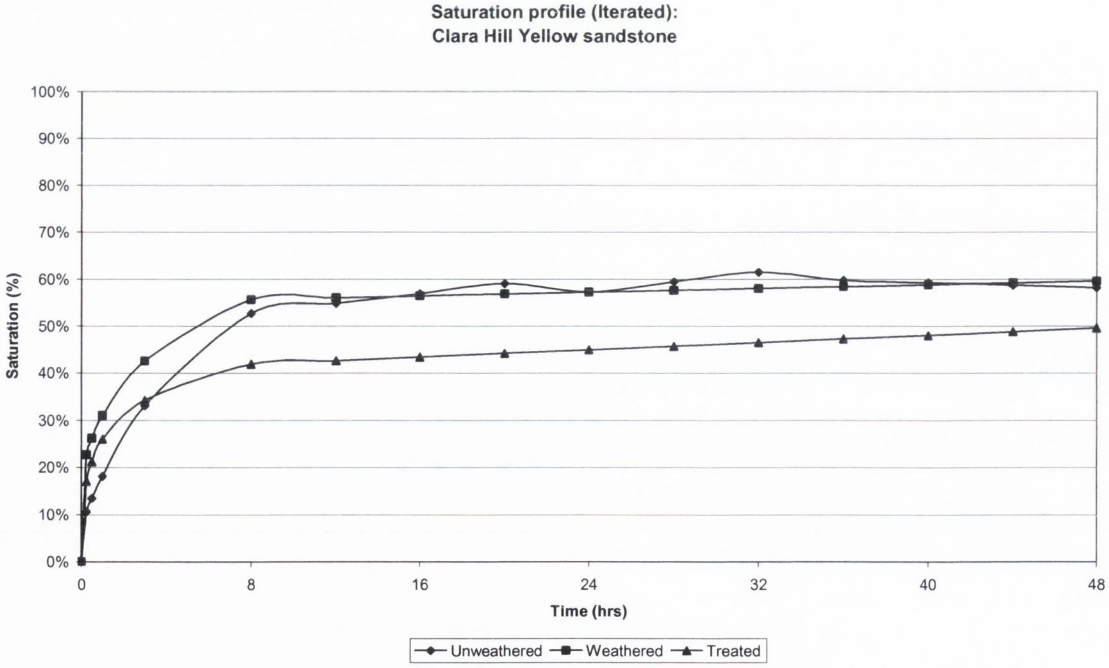

Figure A10-6b: Composed saturation profiles of unweathered, weathered and treated Clara Hill Yellow samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

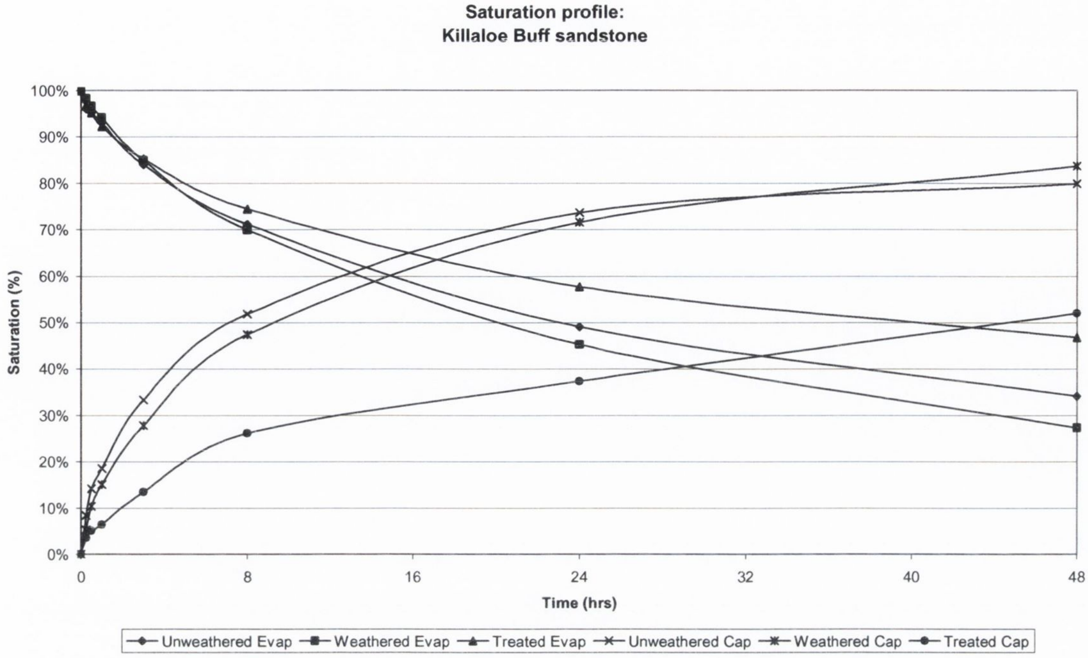

Figure A10-7a: Comparison of saturation profile of treated Killaloe Buff samples during capillary absorption and evaporation with unweathered and weathered profiles

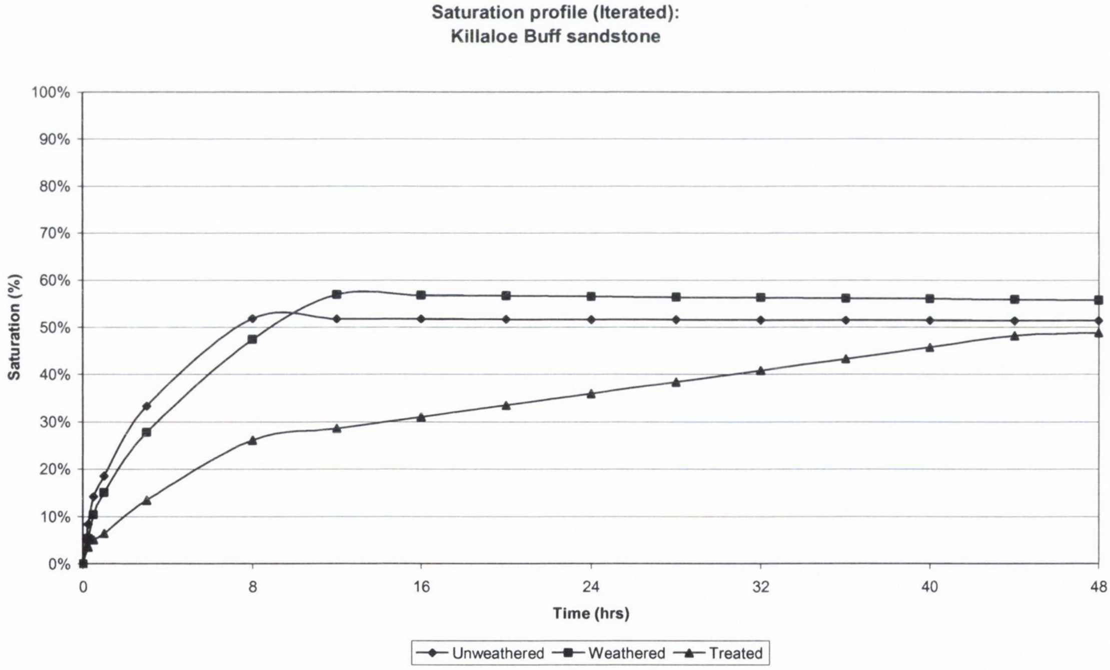

Figure A10-7b: Composed saturation profiles of unweathered, weathered and treated Killaloe Buff samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

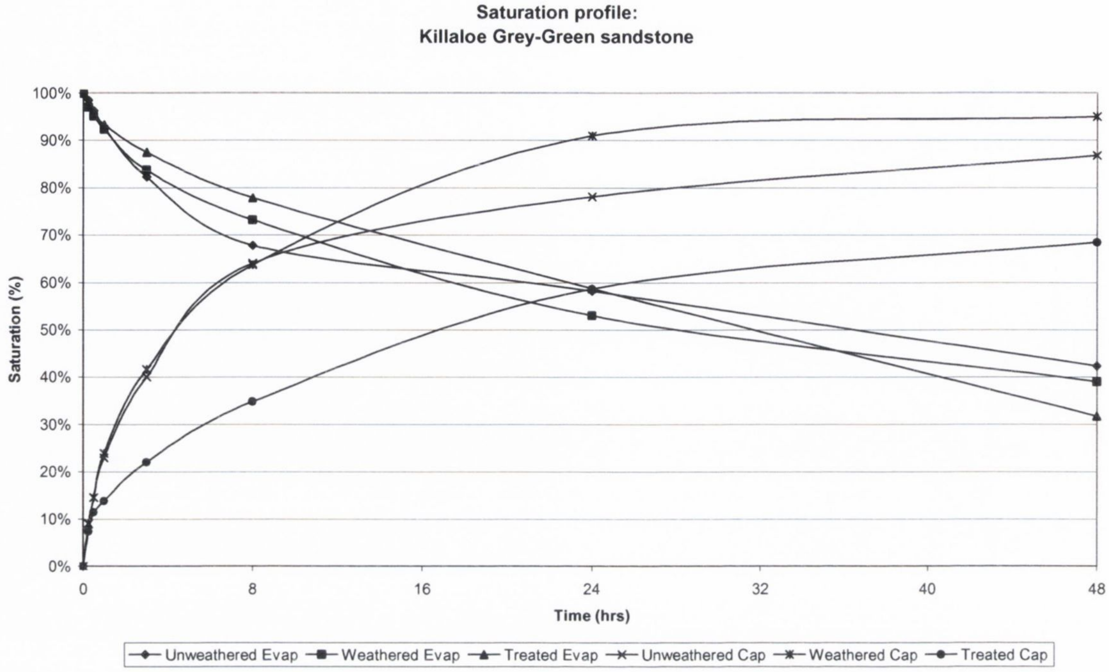

Figure A10-8a: Comparison of saturation profile of treated Killaloe Grey-Green samples during capillary absorption and evaporation with unweathered and weathered profiles

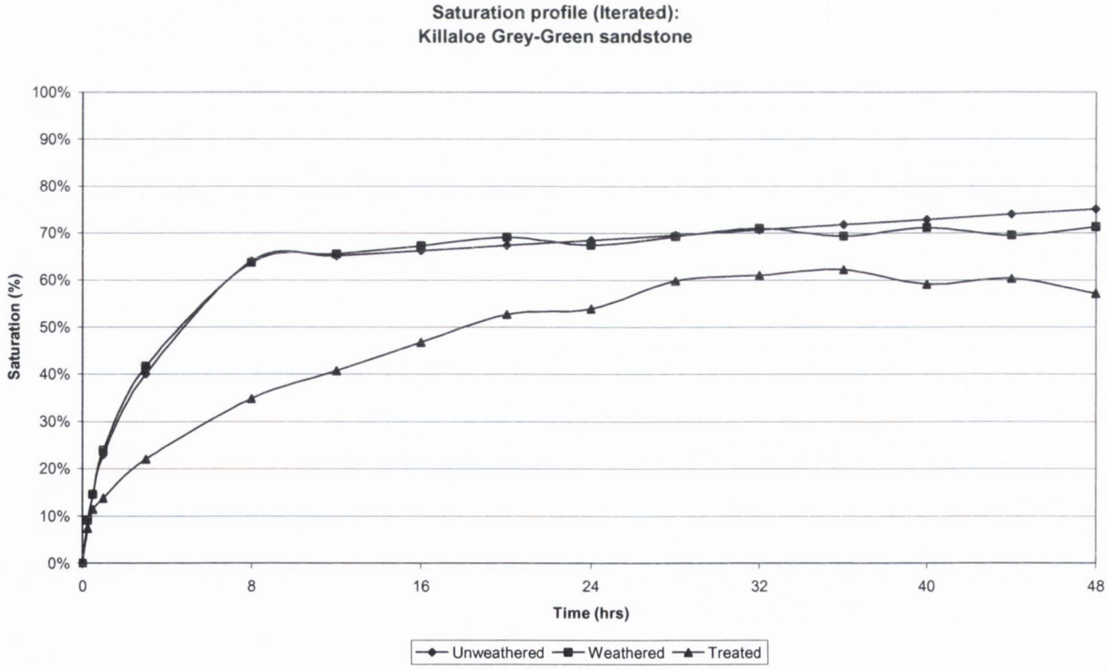

Figure A10-8b: Composed saturation profiles of unweathered, weathered and treated Killaloe Grey-Green samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

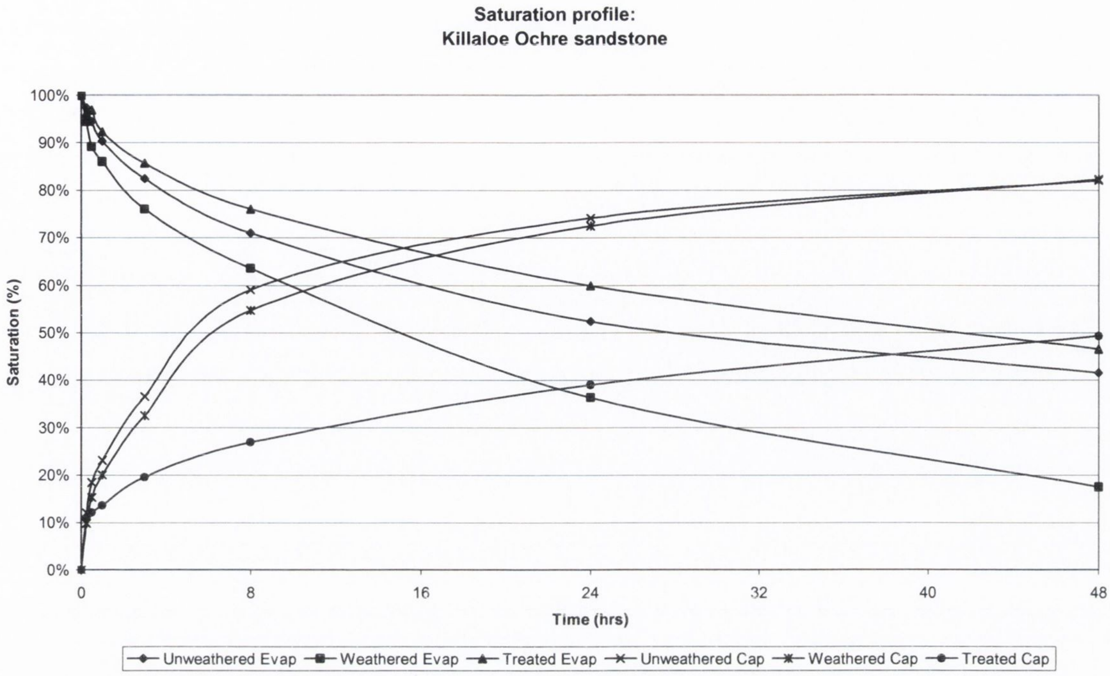

Figure A10-9a: Comparison of saturation profile of treated Killaloe Ochre samples during capillary absorption and evaporation with unweathered and weathered profiles

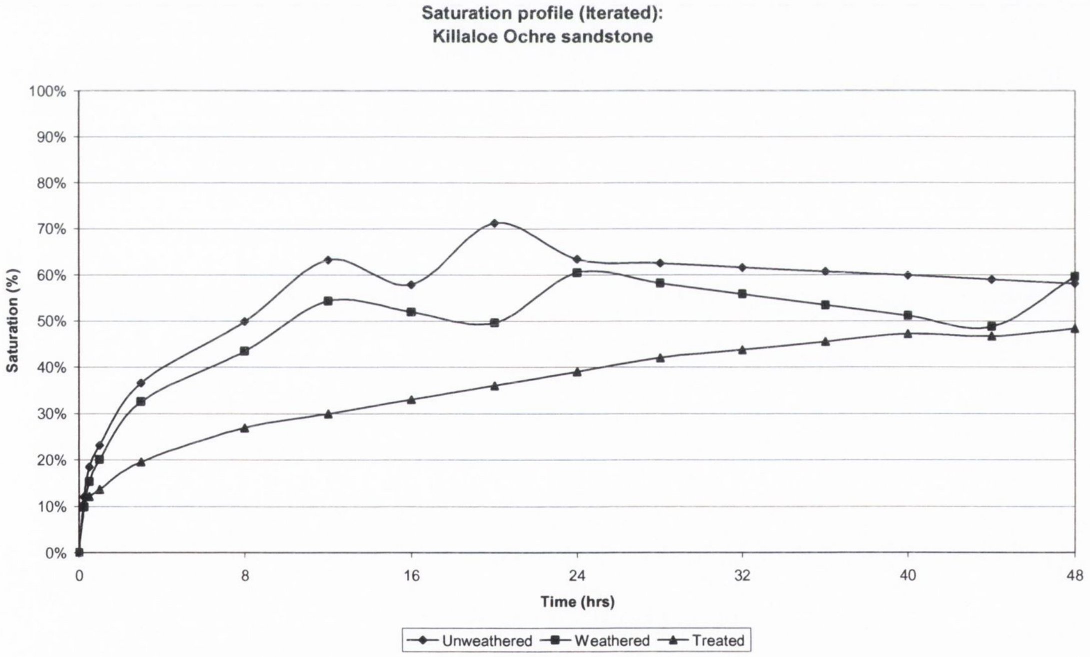

Figure A10-.9b: Composed saturation profiles of unweathered, weathered and treated Killaloe Ochre samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

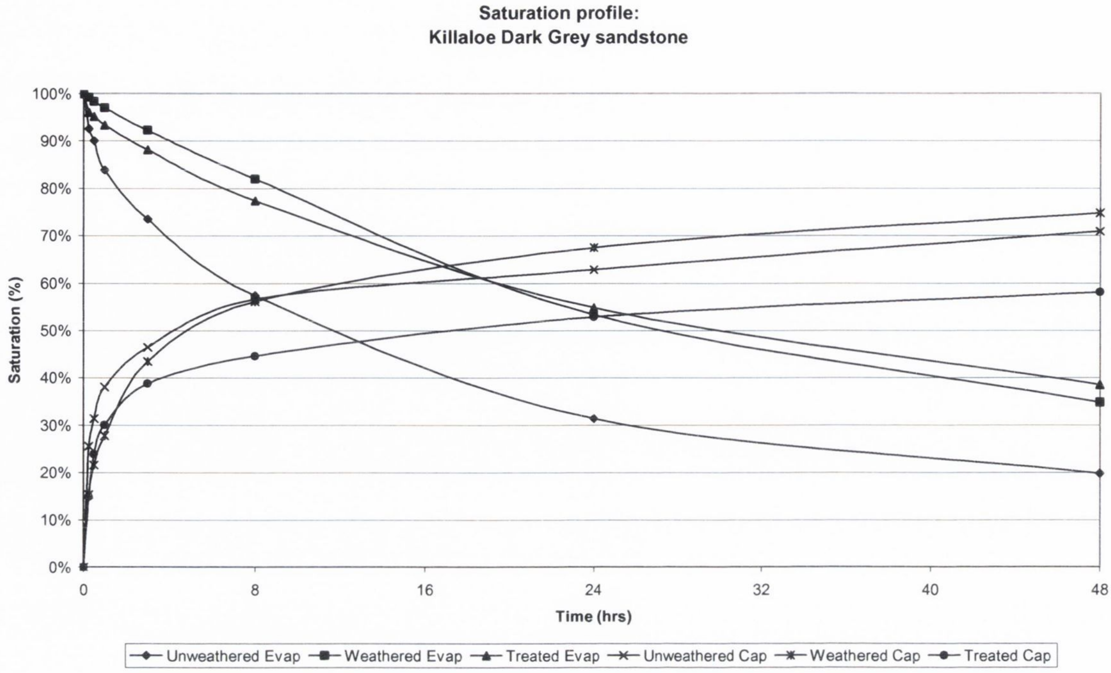

Figure A10-10a: Comparison of saturation profile of treated Killaloe Dark Grey samples during capillary absorption and evaporation with unweathered and weathered profiles

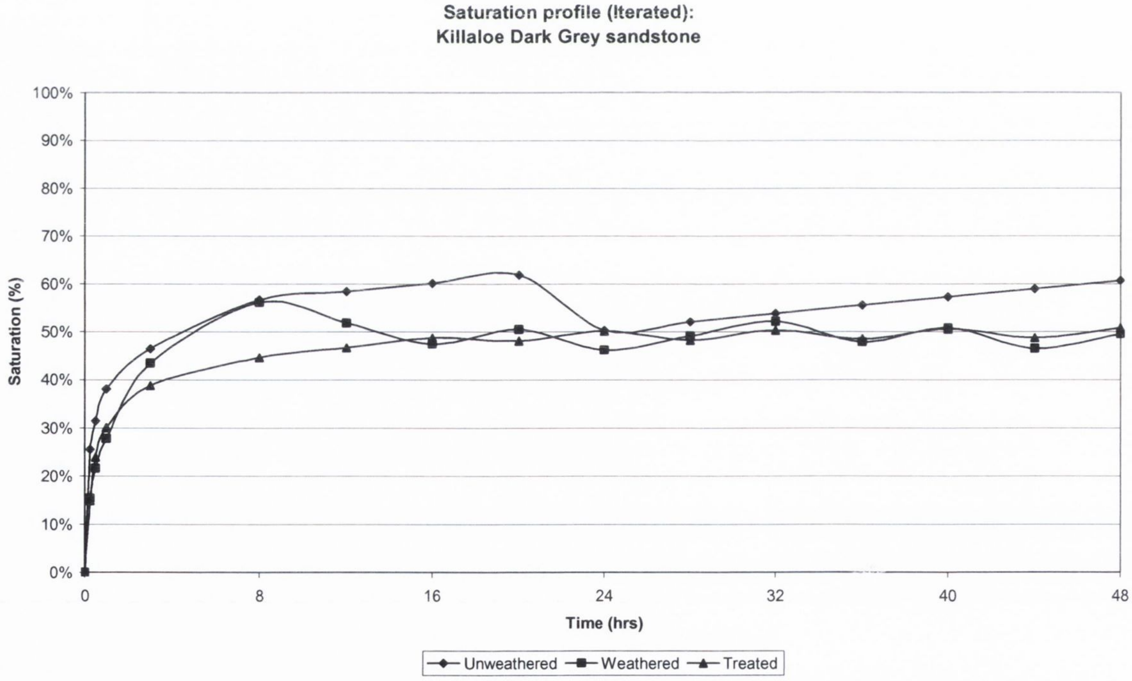

Figure A10-10b: Composed saturation profiles of unweathered, weathered and treated Killaloe Dark Grey samples calculated by iterating progress of capillary absorption and evaporation as functions of saturation (Data points for times >8hrs are based on difference in respective rates)

Appendix 11:

Figures from Hosek & Panek (1985)

Appendix 11: Figures from Hosek & Panek (1985)

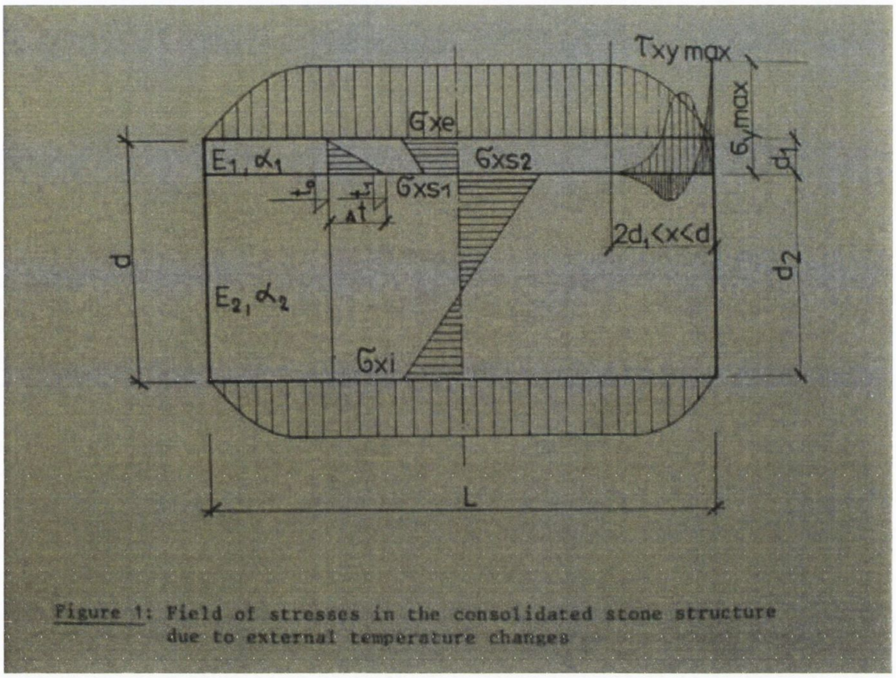

Figure 1: Field of stresses in the consolidated stone structure due to external temperature changes

Figure A11-1: Field of stresses in the consolidated stone structure due to external temperature change

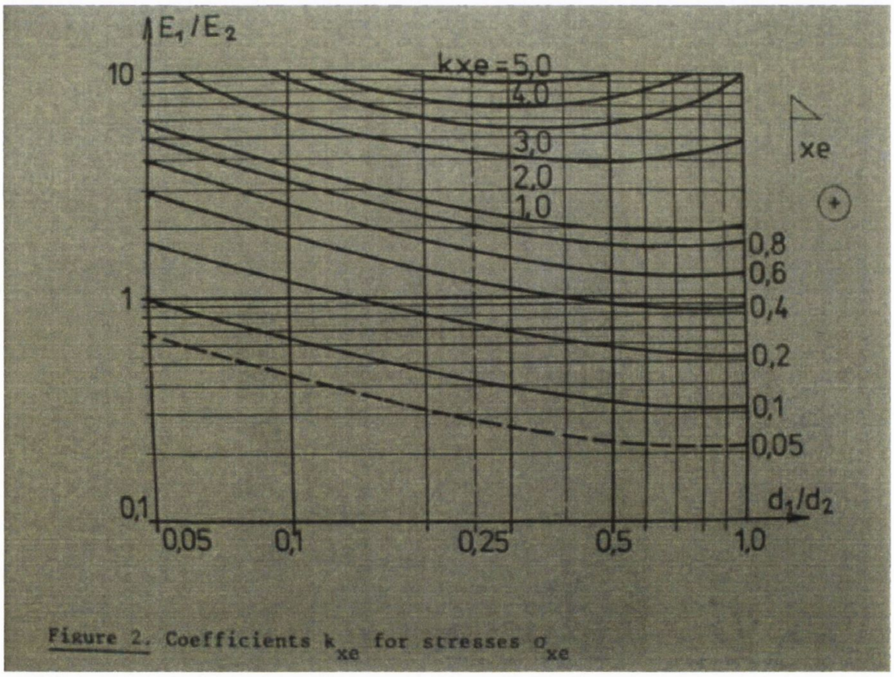

Figure 2. Coefficients k_{xe} for stresses σ_{xe}

Figure A11-2: Coefficients k_{xe} for stresses s $_{xe}$

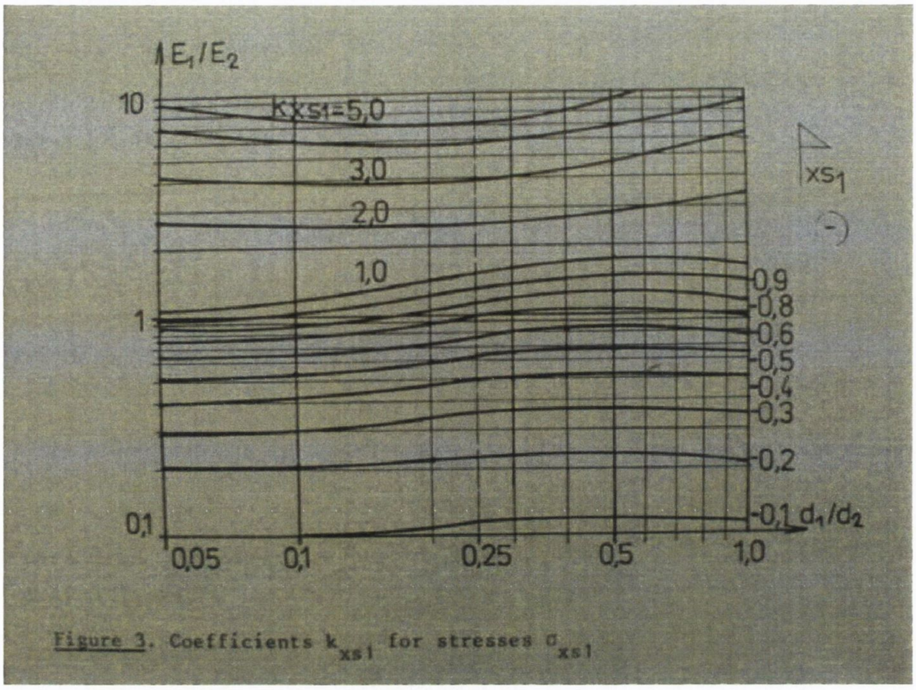

Figure A11-3: Coefficients k_{xs1} for stresses s_{xs1}

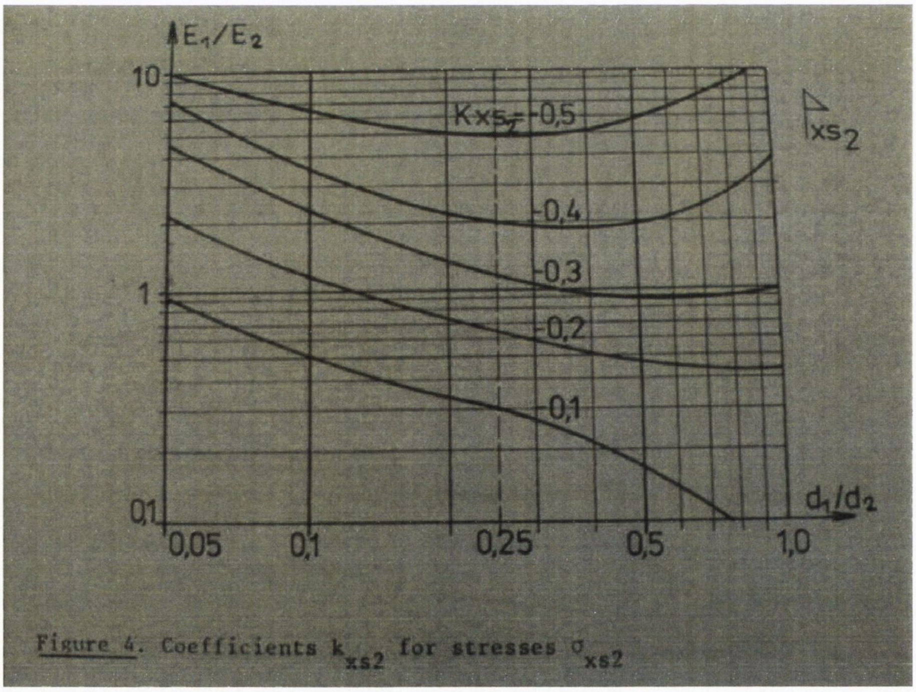

Figure A11-4: Coefficients k_{xs2} for stresses s_{xs2}

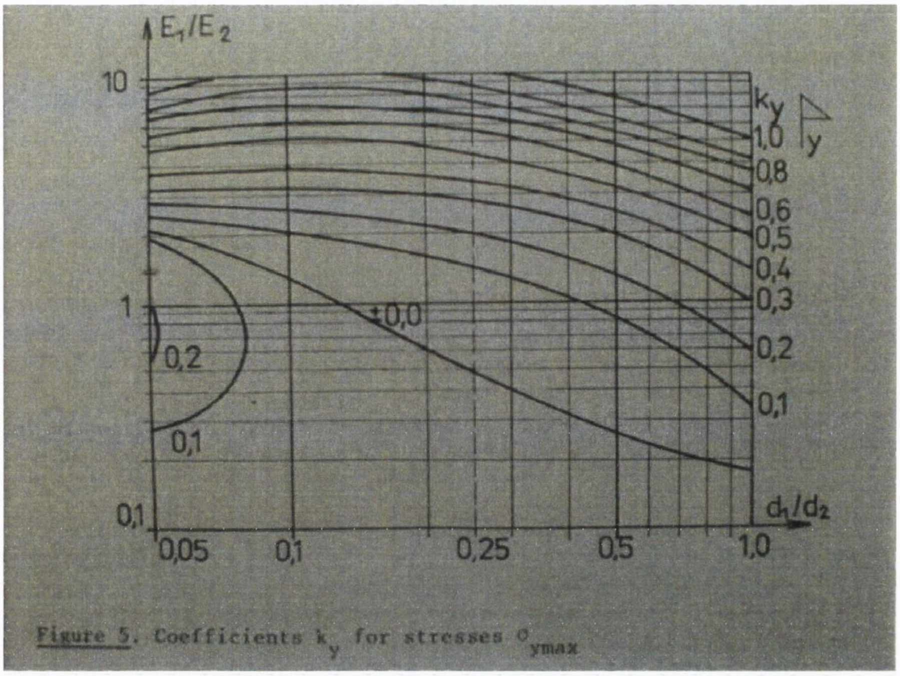

Figure A11-5: Coefficients k_y for stresses s_{ymax}

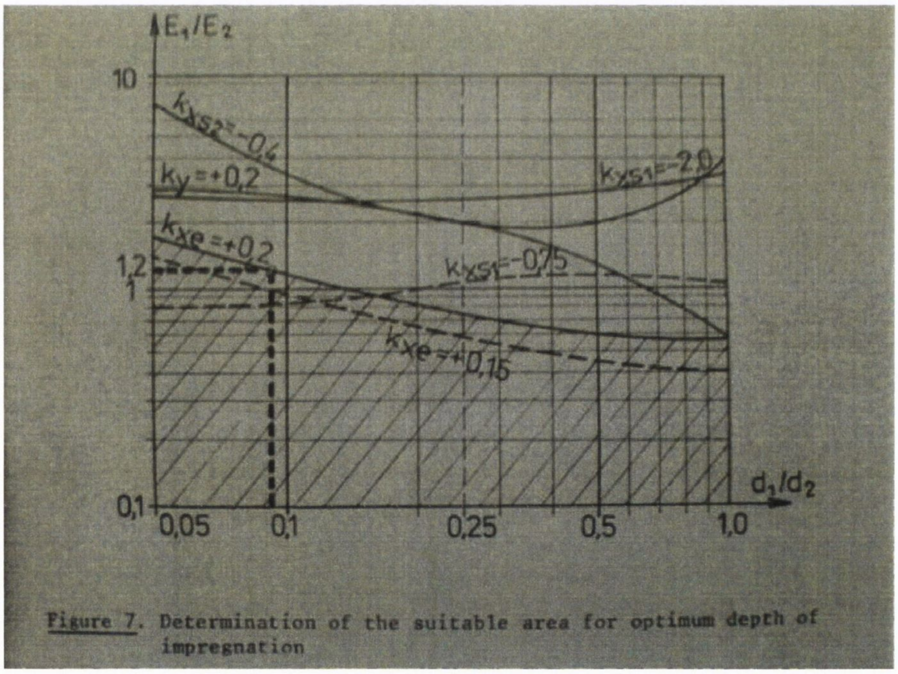

Figure A11-6: Determination of the suitable area for optimum depth of impregnation

Appendix 13:

Recording consolidant treatments

Stone data sheet

Doc. Ref.:

Monument	
Location	

Parties involved in conservation	

Geological information	Source	
	Geological formation	
	Description	
	References	

Petrographic information	Composition		
	Grains	Size	
		Distribution	
	Cements	Type	
		Distribution	
	Pores	Size	
		Shape	
		Distribution	

Laboratory information	Samples	Source		
		Number/Dimensions		
		Appearance		
		Weathering		Units
	Mass structure	Open porosity		
		Apparent density		
	Moisture transfer	Capillary absorption		
		Evaporation		
		Permeability		
	Mechanical strength	Compressive strength		
		Modulus of elasticity		
		Surface hardness		

Exposure data sheet

Doc. Ref.:

Monument	
Location	

Parties involved in conservation	

Construction details	Age of monument	
	Materials	
	Elements	
	References	

Element summary	Masonry walls	Number	
		Orientations	
		Depths	
		Areas	
		Mortars	
	Carvings	Material	
		Detail	
	Exposures	Moisture	
		Wind	
		Sun	

				Units
Environmental information	Climate	Annual Rainfall		
		Driving Rain Index		
		Max Daily Wind Speed		
		Average Daily Sunlight		
		Average Daily Temp		
		Range Daily Temp		
	Moisture availability	Hardstanding		
		Groundwater		
		Parapet/Roofing		
	Salts and deleterious materials	Types		
		Sources		
		Effects		

Treatment record sheet

Doc. Ref.:

Monument	
Location	

Parties involved in conservation	

Compositional details	Product name and composition	
	Degree of polymerisation	
	Catalyst	
	Solvents	
	Nanoparticles	

Stone details	Element	Volume	
		Surface	
		Absorption	
		Pore size distribution	
		Colours	
	Surface	Carvings	
		Roughness	
	Weathering	Material loss	
		Type of loss	
		Visual effects	

Application details	Climate	Temperature	
		Relative humidity	
		Sunshine	
		Wind speed	
		Shelter	
	Volume applied	Start time	
		Start mass	
		End time	
		End mass	
		Evaporation	
	Success	Mass gain per unit area	
		Depth of penetration	