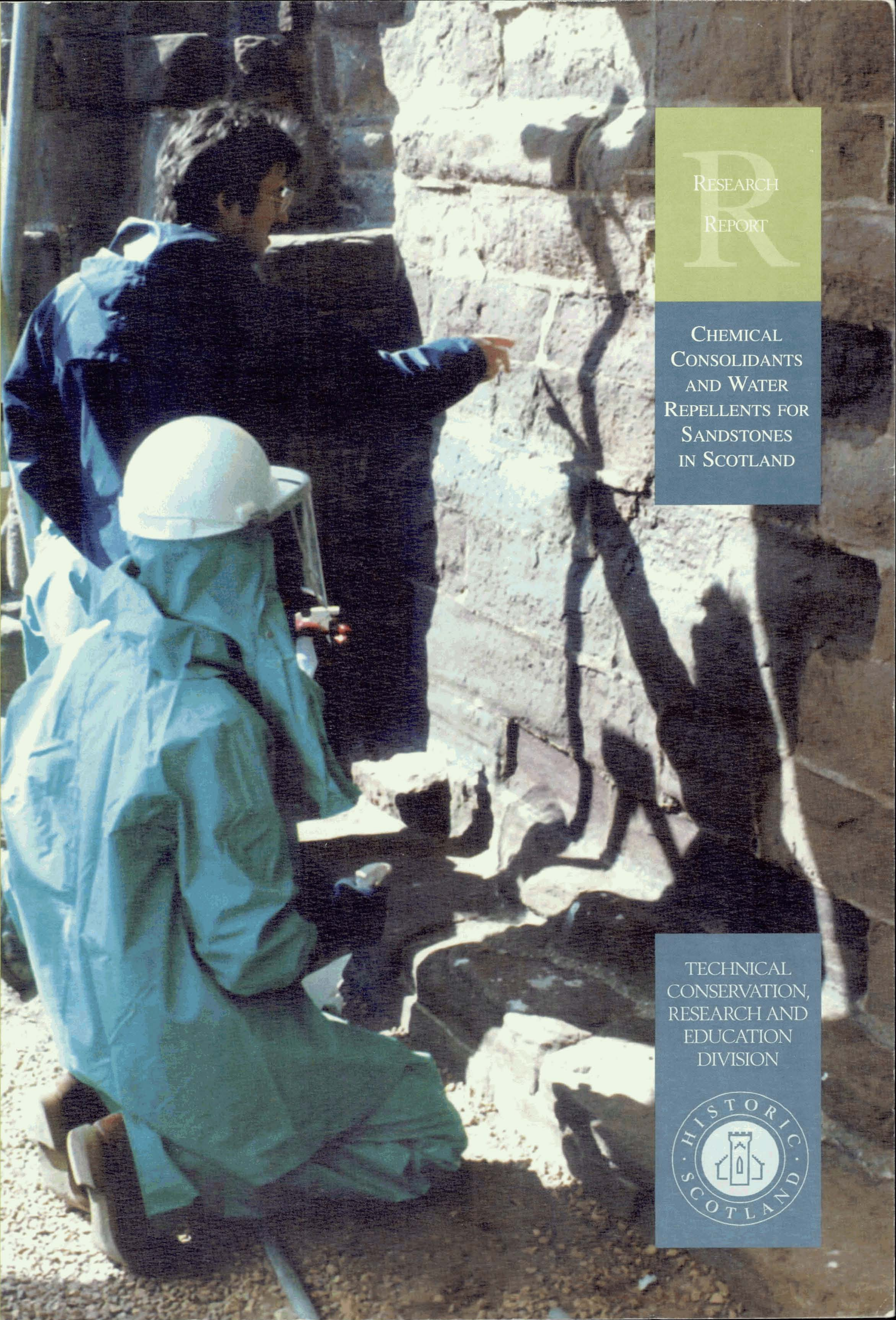

RESEARCH REPORT

CHEMICAL CONSOLIDANTS AND WATER REPELLENTS FOR SANDSTONES IN SCOTLAND

TECHNICAL CONSERVATION, RESEARCH AND EDUCATION DIVISION

HISTORIC SCOTLAND

RESEARCH REPORT

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GUIDES FOR PRACTITIONERS

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2 Conservation of Historic Graveyards (2001)
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CHEMICAL CONSOLIDANTS AND WATER REPELLENTS FOR SANDSTONES IN SCOTLAND

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Published by
Historic Scotland

ISBN 1 903570 20 4

Edinburgh 2003
Commissioned by

TECHNICAL
CONSERVATION,
RESEARCH AND
EDUCATION
DIVISION

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ACKNOWLEDGEMENTS

The Masonry Conservation Research Group at The Robert Gordon University and the Building Research Establishment, Garston gratefully acknowledge the invaluable assistance, advice and understanding provided by the project sponsors throughout the period of this study. In particular Mr Neil Ross and Mr Ingval Maxwell of Historic Scotland.

We also wish to record our thanks to the following individuals and organisations for the assistance they rendered to the project:

Mr Nick Boyce, Historic Scotland

Mr Martin Kirk, Kirk Natural Stone

Mr George Simpson, Stonemason

Mr. Sandy Reid, University of Aberdeen, Department of Geology

British Flowplant Group Ltd

Tensid UK plc

Chemacryl Ltd.

PermaRock Products Ltd.

Remmers UK Ltd.

Wacker Chemicals Ltd.

Degussa Ltd.

Thanks are also due to all those people and organisations, too numerous to list, who have rendered assistance in a variety of forms during the period of the project.

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EXECUTIVE SUMMARY

This report presents the findings of a 2-year project researching the use and effectiveness of consolidants and water repellents on Scottish sandstones. Comprehensive conclusions are contained at the end of the document. Below are the key points drawn from these main conclusions, giving an overview of the work. Also included is a short section explaining the overall impact of this research.

- A consolidant must ideally penetrate past the zone of deterioration (3 to 25 mm) for it to be considered a true consolidant. This research showed limited evidence for substantial increases in tensile strength below 2-15 mm from the surface for any of the consolidants tested.
- The function of the consolidant is to slow natural decay rather than to produce "strength". Sites in Scotland, treated over 20 years ago, show consolidant still present at substantial depth. Additionally, at one site in Arbroath, the original treated surface layers were still present. As this area was evidently substantially decayed at the time of treatment, some protection appears to have been effected.
- Some consolidants may penetrate a few millimetres, others up to 60 mm. The depth of treatment achieved depends as much on the nature of the masonry as the treatment type. For example, Leoch sandstone appears to be impermeable to any of the tested treatments.
- Treament may result in a reduction in the water vapour permeability of a sandstone surface. The maximum decrease in permeability found in during this research was 30%.
- Water repellents may reduce ingress of liquid water through a stone surface but they cannot exclude water which gains access to the stone through cracks, by internal transmission or other mechanisms. Water repellents cannot therefore guarantee to exclude all moisture from masonry.
- A popular method of testing for the presence of consolidants is by water repellency testing (the cheapest method). It is a good test, but not a reliable guide as to the location or extent of consolidation unless comprehensively undertaken with the other tests in this report.
- The type of treatment, the surface to which it is applied and the application methodology governs the degree of discoloration of treated masonry.
- No increase was found in susceptibility to frost damage following treatment with the consolidants or water repellents tested here.
- Emissions of volatile organic compounds from treatments can occur for some weeks following application. These may be flammable if confined and safety precautions must be followed.
- Evaporation, re-distribution and post-application chemical reactions of the applied treatments may occur while setting. This may have the effect of changing the extent and location of consolidation after application.
- The method of application is very important with respect to the depth of penetration of treatment. Depths of application achieved in the field are normally lower than those in the laboratory. For example, application to a vertical wall may pose problems as the treatment may run off the wall before it has a chance to be absorbed. The amount applied and the run-off should always be recorded.

Benefits of the research

- A clear, qualitative and quantitative understanding of what happens when some types of consolidant and water repellent are applied to Scottish sandstones.
- Substantial data on changes to the physical properties of different types of Scottish sandstone due to treatment with consolidants and water repellents.
- Production of recommendations for optimum consolidant characteristics.

- A comprehensive suite of proven tests for analysis of the key issues with respect to the use of consolidants and water repellents, which are of an appropriate scale for real situations.
- Assessment of three historic sites in Scotland 20 years after treatment with consolidants.
- Clear evidence of the presence of silane-based consolidants, without any apparent masonry damage, in Scottish sandstone building surfaces that were treated in the early seventies.
- A proven coring methodology utilising hydraulic coring for sensitive sampling of friable historic surfaces.
- Provision of simulated treated building surfaces in the form of test panels that could be used for further long-term studies.
- A comprehensive, up-to-date literature survey on consolidants and water repellents.

1 INTRODUCTION

Water repellents and consolidants are used in an attempt to minimise the rate of stone decay and to strengthen decayed stone where there has been a failure of the natural stone cement through the normal processes of weathering, the effects of atmospheric pollution or through inappropriate intervention. In the past 20 years many materials have been used with varying degrees of success and no single method has been found to be successful on all stone types.

Where decay has occurred the aim is to preserve the stone, as far as is practicable, in its original state. For this purpose recent research has focused on developing suitable materials for consolidating stone or imparting water repellency. Water repellents are intended to prevent or reduce water penetration into stonework and therefore minimise the rate of decay. Consolidants are intended to strengthen weakened stone and slow the rate of surface loss by binding loosened grains. Knowledge of the medium and long term performance of consolidants and water repellents is minimal and there is a lack of agreement between experts in this field as to which materials can be appropriately used. This casts doubt on the advisability of using these materials on important structures without extensive research and testing.

The present situation with respect to the use of consolidants and water repellents is little different to that stated by Schaffer in 1933.

> *"The causes of the failure of stone preservatives are not far to seek. The properties demanded of a perfect stone preservative are many and conflicting. For instance, a waterproofing agent is required to prevent penetration of moisture, but, at the same time it should allow water, which has gained access at some unprotected point, to escape. A common cause of failure is that, even in porous materials, and under the most favourable conditions, the preservative penetrates only to a small depth and a surface skin is formed which differs in physical properties from the underlying material; dangerous stresses are likely to be set up and ultimately the skin may flake off. The penetration of a preservative solution can only take place when the stone is comparatively dry, which is seldom in this country, and in cases where the deposition of the solid depends on the evaporation of a solvent, the process of drying causes much of the dissolved substances to be drawn back to the surface. Another source of danger is that certain forms of treatment introduce soluble salts as by-products of the reactions involved; these soluble salts may be extremely deleterious."*

(Schaffer, 1933; page 86)

The aim of this programme was to research the effects of modern consolidants and water repellents on Scottish sandstones and their success in reducing the rate of stone decay and of consolidating existing decayed stone surfaces. Specific objectives of the programme were:

1 To compile a literature review of publications relevant to the investigation.

2 To prepare a check list of currently available proprietary materials for the consolidation and water repellent treatment of masonry materials.

3 To assess the principal properties of a range of commercially available stone consolidation and water repellent materials.

4 To identify previously treated stone surfaces and to assess the performance of the treatment.

5 To identify and develop standardised test methodologies for consolidant/water repellent treatments to sandstone, which will simulate the key in-situ parameters and permit realistic comparisons to be made.

6 To undertake experimental investigations to assess the immediate and short-term effects of the application of a range of consolidant and water repellent treatments to a representative range of sandstones used in Scottish buildings and monuments.

7 To assess the optimum depth of penetration for the consolidation of sandstone and to make comparisons with depth of penetration of existing treatments on buildings.

8 To initiate new field experiments to act as a basis for future monitoring and assessment of the medium and long term performance of a selected sample of consolidant and water repellent materials.

9 To identify and report on areas in need of further associated research resulting from the study.

Sandstone characteristics can vary widely between sandstone types and even between blocks of the same stone from different parts of the quarry. The results of different treatments may also vary widely. As a result, the research focuses on selected consolidants and water repellents which are or have been used in Scotland and tests them on a range of sandstones (both soiled and fresh) which are commonly used as building stone in Scotland.

The research programme was commissioned by Historic Scotland and was a collaborative project involving both The Robert Gordon University (Aberdeen) and the Building Research Establishment (Watford).

2 LITERATURE REVIEW

Conservation of existing stonework may not always be practicable and where severe stone decay has occurred on historically important or valuable buildings or monuments it may be necessary to replace the decayed stone with new stone or some alternative material. Glasgow West Conservation Trust (1993) in their tenets of good practice, note that with respect to stonework, maintenance is more desirable than repair, and repair is more desirable than replacement. The Edinburgh New Town Conservation Committee (ENTCC) (Clark, pers. comm.; Davey *et al.*, 1978) suggest that plastic repairs (i.e. use of mortar mixes to recreate stone detail where loss has occurred) may be used on elaborate features or on insignificant areas of masonry walling, where they will not be too obvious in comparison with the natural stone, and that any larger areas of decay should be repaired by replacement or indenting, although this will result in the loss of the original stone. Large scale plastic repairs are generally avoided. Repairs in natural stone are preferred to plastic repair and the ENTCC actively discourage plastic repairs unless they are used to extend the life of a stone and are on very small areas (Clark, pers. comm.). Historic Scotland (1998) recommends that severely damaged or decayed stone in listed buildings should be replaced or, in certain circumstances, indented. Plastic repairs are avoided as far as possible.

> *"If an individual stone is damaged or decayed to the point that its structural integrity is in doubt, the whole stone should be cut out and replaced in matching natural stonework. Repairs involving partial indenting should not normally be considered. In certain circumstances small indents may be appropriate on moulded detail, but even here leaving the damaged stonework may be more acceptable than carrying out a visually intrusive repair."*
>
> Historic Scotland (1998, p92).

> *"Extensive 'plastic' repair work should not be permitted unless the facade has already been painted and is in such a condition that it must remain so. Patching using specialised mortars may, however, be acceptable in cases where it is important to cut out as little as possible of the original stonework. It may therefore be appropriate for small scale repairs to moulded or sculptured details, particularly where the stonework is at high level and the nature of the repair will be less obvious."*
>
> Historic Scotland (1998, p93).

2.1 Polymers

Organic polymers (i.e. carbon-based polymers) have been used as water repellents and in stone consolidation although it has recently become more common to use silanes (i.e. silicon-based polymers). Both organic polymers and silanes have also been used in some relatively small scale tests in the production of materials for plastic repairs.

Polymers are large molecules built up from many identical smaller units (monomers). Polymers differ in their properties depending on the chemical composition of the monomers and on how they link together. Monomers which link end to end form long chains. Those which can form more than two links can form branched chains which may cross-link with other chains in a variety of ways from slight cross-linking to complex interwoven networks (Figure 1).

Polymers which are unbranched or only slightly branched are thermoplastic. That is, when heated the molecules can flow past each other and the material can be shaped on heating. If the cross-linking is more extensive, a thermosetting material is formed which may soften on heating but cannot achieve a permanent change of shape (Horie, 1987).

Glass transition temperature (T_g) is the temperature at which the polymer is in transition between a soft and a glassy state. A polymer which is too soft at its working temperature may flow or pick up dirt. A polymer which is too stiff may crack under stress. Time scale affects the T_g and, over long time periods, the T_g is effectively lower than the value measured over a relatively short time scale. This means that over long time periods polymers which appear hard may flow and pick up dirt. The T_g may be raised or lowered by increasing or decreasing the polymer chain length. The T_g may also be lowered by incorporating low molecular weight additives such as solvents (plasticizers), although over time these additives are gradually lost from the material. For highly cross-linked polymers above the T_g, the polymer will not flow or change shape since the molecules cannot move past each other but it can soften, becoming rubbery. The properties of highly cross-linked polymers do not change very much as the temperature is raised above the T_g. If the degree of cross-linking is very high (e.g. with formaldehyde resins or silanes) the T_g disappears altogether (Figure 2). For some polymers (e.g. polyethylene or wax) where the polymer is partially made up of crystals, the polymer does not liquify above T_g until the temperature reaches the melting point (T_m) (Horie, 1987).

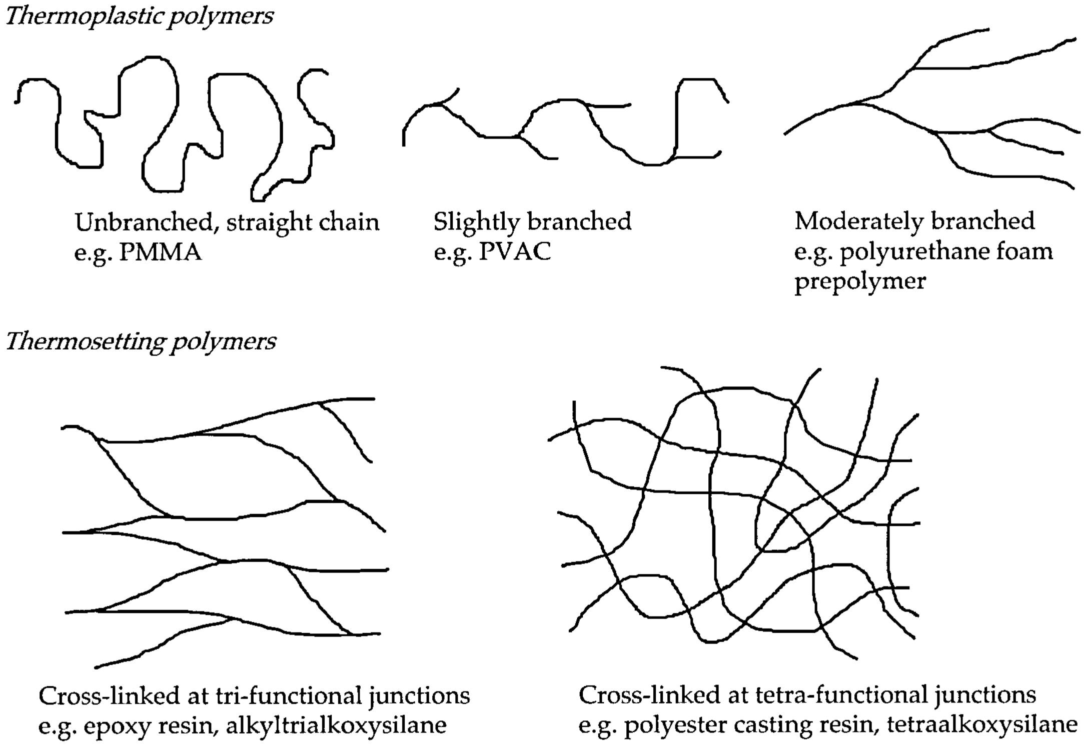


Figure 1 Examples of polymer branching (after Horie, 1987).

The mechanical properties of polymers are controlled by a number of factors including glass transition temperature, molecular weight, the presence of crystals, the age of the polymer and the method of preparation. The physical properties of a polymer must be matched to its use. If the underlying material expands and contracts to a greater degree than the polymer is capable of then the polymer may fracture or deform. If the polymer is too strong and requires a large force to stretch it then it may detach from the underlying material (Horie, 1987).

Organic polymers may deteriorate through the action of light (especially UV radiation), heat and oxygen by a variety of mechanisms including becoming insoluble, yellowing, cracking, weakening, shrinking, expanding, flowing, becoming soiled or reacting with the object they are applied to. Polymer flow and attraction of soiling are due to the physical properties of the polymer, most other deterioration is caused by chemical alteration. The inclusion of certain pigments can increase the rate of ageing of polymers. The presence of gaseous pollutants, such as ozone or oxides of sulphur and nitrogen, can also increase the rate of decay (Horie, 1987).

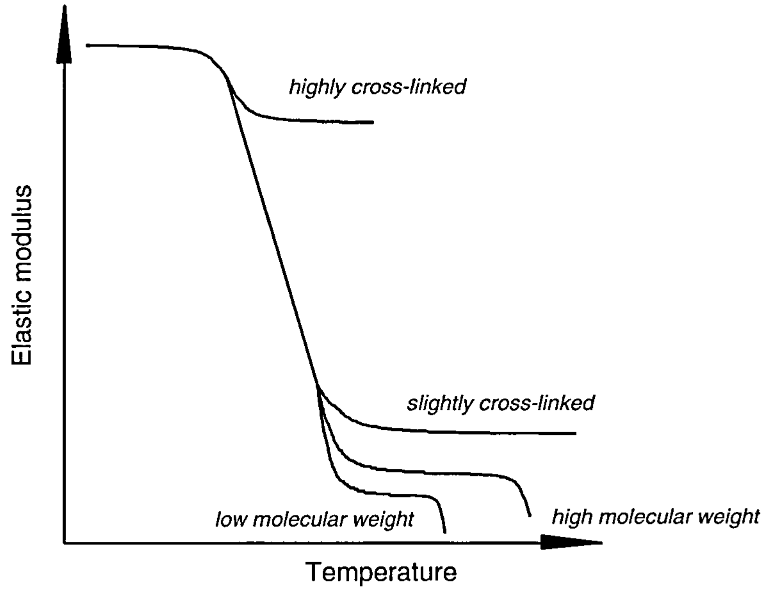


Figure 2 Effects of cross-linking and molecular weight on the glass transition temperature (Tg) of polymers (after Horie, 1987).

Polymer adhesion is greatest where the polymer film is able to cover all the underlying solid material. Ideally, the polymer should remain liquid for a relatively long time to allow penetration of the liquid into pores and crevices (Price, 1981; Sasse *et al.*, 1993).

Setting of a polymer may be achieved in various ways depending on its type but setting will always involve some reduction in volume. Cross-linking resins set by transforming from liquid to gel to solid. Materials which set by cooling may precipitate crystals or form relatively stable inter-molecular bonds. For materials which set by the evaporation of solvents, the glass transition temperature rises as the solvent evaporates and the material will set when the T_g rises above the ambient temperature. Emulsions set when the particles coalesce (Horie, 1987).

After the material has formed a gel, it cannot flow to accommodate changes in shape. Therefore, as a polymer shrinks on setting, tensions may be set up which can reduce the life span of the polymer. The amount of stress can be minimised if the ambient temperature is close to the T_g.

2.2 Water repellents and consolidants

Water repellents and consolidants are used in an attempt to reduce the rate of stone decay and to strengthen decayed stone where there has been failure of the natural stone cement. Many materials have been used with various degrees of success and no single method has been found to be successful on all stone types. There are a large number of studies involving a wide variety of testing methods, consolidants, water repellents and stone types, however, the information which can be gathered has little overall structure or general applicability although some workers in this field have put forward ideas to co-ordinate investigations (Boyer, 1987; De Witte, 1989; Pien 1989). Information summarised from a variety of recent papers on consolidants and water repellents can be found in Table 38, Section 9. Most studies have been aimed at finding a suitable treatment in one particular situation and little information exists which would give guidance on matching water repellents or consolidants to specific physical or chemical attributes of the underlying stone.

In general, if a consolidant or water repellent is to perform adequately there are certain criteria that must be met. The consolidant or water repellent should:

- be compatible with the stone type.
- have good adhesion.
- penetrate the stone to at least 25 mm (Price 1975, 1981; Richardson, 1995) or to the depth of stone deterioration (Boyer, 1987; Lewin and Wheeler, 1985; Torraca, 1976; Zinsmeister *et al.*, 1988) to avoid forming a thin surface coating with different characteristics to the body of the stone. There is some disagreement (see also Section 2.2.1) in the literature as to whether water repellents in particular should be confined to the immediate surface (Šrámek, 1993) or whether they should penetrate the stone more deeply (Price 1975, 1981).
- have low viscosity (less than about 10 mPa.s (Littmann *et al.*, 1993; Sasse *et al.*, 1993) or 3 cP (Lewin and Wheeler, 1985)), moderate surface tension (between about 20 mNm^{-1} and 30 mNm^{-1}), low average molecular weight and low reactivity within the first few hours, that is, little increase in viscosity during this time (Sasse *et al.*, 1993). All these factors should increase the penetration of the material into the stone although materials with too low a molecular weight may be drawn back towards the surface on evaporation of the solvent (Domaslowski and Strzelczyk, 1993). Volatile monomers may be lost by evaporation before polymerisation can occur (Lewin and Wheeler, 1985).
- be capable of withstanding the full range of temperature variations likely to be encountered on a building facade (Sasse et al., 1993).
- not block the porosity of the stone or significantly reduce the rate of moisture transport through the stone (Frediani *et al.*, 1992; Moropoulou *et al.*, 1992; Rossi-Manaresi, 1981; Zinsmeister *et al.*, 1988). There is some disagreement in the literature about whether water repellent materials which cause evaporation of water to take place within the body of the stone at the boundary between treated and untreated stone may or may not accelerate decay (De Witte and Bos, 1992; Šrámek, 1993).
- not alter the porosity such as to make the stone vulnerable to freeze-thaw damage (Clifton, 1984). Stones types in which much of the pore space is in the form of micropores (i.e. $<5\ \mu m$) are more vulnerable to freeze-thaw damage.
- when applied to deteriorated stone, alter it so as to match as closely as possible the physical properties of sound stone (e.g. colour, thermal expansion, porosity, etc.) (Boyer, 1987).
- not cause colour or reflectance changes to the stone surface and should not discolour over time. That is, the material should not change colour due to degradation by light, temperature changes or oxidation.
- not be vulnerable to decay by salts, acids in rain water, atmospheric gases and pollutants (Ciabach and Lukaszewicz, 1993) or biological organisms (Krumbein *et al.*, 1993).
- weather at a similar rate to the sound stone.
- have a low solvent content (for health and ecological reasons). In a number of countries including USA, Sweden and Switzerland the large scale use of volatile organic solvents is, or will soon be, banned.

2.2.1 Water repellents

Water repellents are intended to prevent or reduce water penetration into stonework and so reduce the rate of decay. It has also been suggested (Nishiura *et al.*, 1984) that water repellents will reduce the vulnerability of a stone to frost damage since the water repellent treatment will reduce the ability of water to flow through a stone to the freezing front.

A number of authors have reported successful treatments with water repellents (Ashurst and Dimes, 1990; Ciabach and Lukaszewicz, 1993; Guidetti *et al.*, 1992; Manganelli del Fa' *et al.*, 1981; Piacenti *et al.*, 1985, 1992, 1993; Rossi-Manaresi, 1981; Šrámek and Králová, 1981; Villegas and Vale, 1992).

Other authors have not found water repellent treatments to be successful. Clarke and Ashurst (1972) found that, of 68 examples where silicone-based water repellents had been used, in over 90% of cases the rate of stone decay was unchanged or faster than untreated surfaces and in no cases was there a significant reduction in the rate of decay relative to control panels. De Witte and Bos (1992) found that while some water repellents impart resistance to damage caused by acid rain they can increase the rate of decay due to acid mists. Šrámek (1993) investigated, using radioactive labelling (see Section 2.3.2), the effects of water repellent agents on the decay rates of stones subjected to pollutant gases in humid conditions. He has found (Šrámek, 1993) that hydrophobic treatments do not significantly affect decay rates due to pollutant gases such as SO_2. Since hydrophobic treatments can prevent the ingress of liquid water but do not affect the absorption of vapour in the body of the stone, pollutants can still gain access to the stone interior and the rate of decay may be increased at the boundary between treated and untreated stone. Šrámek (1993) suggests that since water repellent treatments can only be effective at preventing the ingress of liquid water they should only be applied to the immediate surface to avoid the possibility of causing decay internal to the stone.

The greatest danger with water repellent treatments is that, where the surface porosity and permeability is significantly reduced, moisture which gains access to the stone may be trapped behind the treated layer and lead to rapid decay and spalling due to frost damage, salt deposition or changes to the binding materials in the stone. Even where the porosity and permeability are not greatly reduced, liquid water from the interior of the stone will still be prevented by the water repellent coating from moving out to evaporate at its surface and will evaporate from behind the treated layer. This may lead to salts being deposited in this area and, in the longer term, can lead to spalling of the surface (De Witte and Bos, 1992; Šrámek, 1993). Spalling of the treated layer may also be enhanced by stresses caused by differences in its thermal behaviour compared to untreated stone (Price, 1975). It has been suggested (Price, 1975) that water repellent treatments would need to be at least 25 mm thick to avoid this danger. This is at odds with the findings of Šrámek (1993) who suggested that water repellent treatments should be confined to the immediate outer surface. It is possible that both superficial and deep treatments would both avoid the problems of enhanced rates of decay which occur with treatments of a few millimetres depth. While the superficial treatment would avoid causing decay by not trapping moisture at depth in the stone, the deeper impregnation might be of sufficient thickness to prevent ingress of water vapour to untreated areas of stone.

Waxes (Ashurst and Dimes, 1990) and linseed oil (Dukes, 1972) have been used in the past as water repellents and waterproofers. However, it is often difficult to achieve deep penetration or adequate water repellency. In addition, waxes and oils discolour the stone and yellow over time and the surface picks up dirt. In the longer term the surface may suffer from break-through of salt efflorescences and the whole treated surface may break away (Ashurst and Dimes, 1990). On sandstones, silane-based repellents can be successful (Ashurst and Dimes, 1990). Silanes are often used as consolidants but those with attached alkyl groups also have some water repellency (Ashurst and Dimes, 1990; Rossi-Manaresi, 1981; Šrámek, 1993; Šrámek and Králová, 1981; Wheeler *et al.*, 1992). Polyurethanes have also been tested as water repellents with variable success (Auras, 1993; Guidetti *et al.*, 1992; Rossi-Manaresi, 1981; Valdeón *et al.*, 1992). Perfluoropolyethers are often used as water repellents and many studies have reported good results (Angel Bello *et al.*, 1992; Frediani *et al.*, 1982; Manganelli del Fa' *et al.*, 1981; Piacenti *et al.*, 1985, 1992, 1993; Rossi-Manaresi, 1981). Perfluoropolyether application is theoretically reversible by the use of fluorinated solvents (Frediani *et al.*, 1982) although removal of this material from a building facade might present practical difficulties. Perfluoropolyethers, unlike many other treatments, are not reported to cause colour changes to the stone (Ashurst and Dimes, 1990; Manganelli del Fa', 1985; Tiano *et al.*, 1985).

The effectiveness of both water repellents and consolidants declines over time. This is especially the case with perfluoropolyethers which remain mobile within the stone. Snethlage *et al.* (1989) surveyed 35 buildings in Germany which had had water repellents applied to the stone in the past. They found that, in many cases, the degree of water repellency had declined greatly over 10-15 years. Butlin *et al.* (1989) found that over 12 years the effectiveness of preservative treatments on limestones declined until weight losses were indistinguishable from those on control samples.

A previous treatment with a water repellent may reduce penetration of a later consolidant treatment although consolidants with organic solvents may penetrate much better than those using water as a solvent (Dukes, 1972).

2.2.2 Consolidants

Consolidants are intended to strengthen weakened stone and slow the rate of surface loss by binding loosened stone through bridging of gaps between grains (Häberl, 1991; Sasse and Honsinger, 1989; Sasse *et al.*, 1993). Some consolidants also have water repellent properties. Consolidants are normally applied in a fluid state to allow penetration into the stone. The applied fluid may solidify by cooling or it may set by chemical reaction or by evaporation of solvents. There is normally a reduction in volume on setting which, depending on the method used, may be large or small and can result in stresses being set up in the stone if the material adheres to the mineral grains before shrinkage is complete (Lewin and Wheeler, 1985). Some of these materials may alter as they age, through the action of light, heat, moisture, physical or chemical attack or the action of biological organisms, and this can alter the properties of the material (Horie, 1987; Palma Dias, 1992).

Problems may arise where consolidants are used inappropriately or are applied incorrectly. Insufficient penetration, blockage of pores or reduction in water or water vapour transport rates can result in the spalling of the stone surface due to differences in its physical properties (e.g. thermal expansion) or to deposition of damaging salts within the stone (Boyer, 1987; Clifton, 1980; Palma Dias, 1992; Piacenti *et al.*, 1995; Price, 1981; Sasse *et al.*, 1993; Šrámek, 1993). While results of consolidation may appear good in the short term, in the longer term some investigators have found that decay can be more rapid than if the stone had been left untreated (Boyer, 1987; Delgado Rodrigues, 1993).

Many stone consolidants also have some water repellent properties (i.e. silanes with attached alkyl groups). Although many researchers in this field have reported good results from such consolidants (e.g. Ciabach and Lukaszewicz, 1993; Guidetti *et al.*, 1992; Price, 1981; Saleh *et al.*, 1992; Villegas and Vale, 1992; Wheeler *et al.*, 1992), others have concerns that, where moisture, which will inevitably gain access to the interior of treated stones, accumulates and is forced to evaporate from behind the outer surface of the stone, deposition of soluble salts or frost damage may result in surface spalling (De Witte and Bos, 1992; Šrámek, 1993).

There are a number of other complications that may arise with consolidation of stone. If the consolidant increases the proportion of fine pores, this can result in increased susceptibility to frost damage (Dukes, 1972). De Witte and Bos (1992) suggest that penetration of consolidants below damaged stone into sound stone could result in the production of a hardened layer which may impede moisture loss. Since treated areas may weather differently to untreated areas it may be advisable to treat the whole of a structure rather than one part (Clifton, 1980). Inadequate consolidation of the outer surface of stone may result where solvent evaporates relatively rapidly from the surface (Auras, 1993). Where a stone is heavily contaminated with salts, consolidation may be ineffective (Price, 1981).

Consolidants that are applied partially or completely pre-polymerised must be dissolved in solvents to give them a low enough viscosity to penetrate the stone. The polymers are deposited as the solvent evaporates (Clifton, 1980; Lewin and Papadimitriou, 1981). The rate of evaporation of the solvent is important as, if the evaporation is too rapid, the consolidants may be drawn back to the surface and deposited there in a thin layer (Lewin and Papadimitriou, 1981; Munnikendam, 1967, 1973). This can lead to spalling of the surface if the consolidant forms an impervious layer or if it differs in character from the underlying stone (Clifton, 1980). For this reason the use of consolidants which are deposited by evaporation of solvents is not recommended by some authors (Munnikendam, 1970).

Even within one building, the characteristics of sandstones can vary widely from block to block and the results of consolidation may also vary widely. Snethlage *et al.* (1989) found that they could differentiate between different characteristics of the same sandstone in one building and that while in some cases application of a consolidant resulted in strengthening of the outer weakened surface, in other cases the surface was over-strengthened and in a third case the consolidated stone strength was homogeneous with depth. A homogeneous depth profile is, of course, the most desirable outcome of consolidation with respect to stone strength.

2.2.3 Materials used as consolidants and water repellents

2.2.3.1 Silane-based materials

These include a wide variety of organosilicon compounds which polymerise inside the stone. In order to form a polymer that can function as a consolidant, it is necessary that the monomer should have three or four reactive groups (Lewin and Wheeler, 1985). This allows the polymer to form cross-links and create a network. The polymerisation reaction of silanes requires the presence of water (Brethane uses an organo-metallic catalyst instead of water. The treatment is partially polymerised before application and does not need any moisture to work although reaction products may include water). If there is a lack of water then hydration will not proceed to completion and much of the consolidant may be lost in evaporation (Charola *et al.*, 1984a). Polymerisation is faster at higher relative humidities (Charola *et al.*, 1984a), however, faster polymerisation may result in the accumulation of stresses in the polymer (due to the viscous nature of the intermediate silanols (Figure 3)) which may later result in cracking (Charola *et al.*, 1984a). The amount of water present in the stone is therefore critical to the outcome. Charola *et al.* (1984a) recommend that, in curing of methyl trimethoxysilane, the relative humidity should be between 30 and 50% RH.

In order to avoid the potential problems inherent in using only the water present in the environment to effect polymerisation, many application methods use mixtures of water and silane. Since the solubility of water and silanes in each other is small, an additional substance must be added to make them miscible (e.g. ethanol or acid (N.B. acids will be neutralised in calcareous stones)). Richardson (1995) notes that (with tetraethoxysilanes) only polar solvents should be used since the use of non-polar solvents (e.g. white spirit or kerosene) resulted in the formation of amorphous or microcrystalline silica with very poor consolidation. In some cases a catalyst (e.g. an organo-metallic compound or potassium hydroxide) is also used to initiate the reaction (N.B. some catalysts, e.g. alkalis, may be damaging to stone). Lewin and Wheeler (1985) recommend a water to silane molar ratio of at least 2 : 1 to lead to gelation. Lewin and Wheeler (1985) also found that the order of mixing was important and that more predictable results were obtained when mixing silane into a water-alcohol solution rather than mixing water into a silane-alcohol solution.

The theoretical end product of polymerisation is deposition of silica (although trialkoxysilanes will form a polymer containing other functional groups) similar to the natural silica deposits which bind many sandstones. Large strength improvements have been achieved using silanes (Arnold et al. 1976; Bosch, 1972; Caselli and Kagi, 1995; Danehey *et al.*, 1992; Lukaszewicz *et al.*, 1995; Saleh *et al.*, 1992; Snethlage *et al.*, 1989; Wheeler *et al.*, 1992; Zinsmeister *et al.*, 1988). The polymer produced by this reaction is very stable and will not break down in UV light or when exposed to acid rain as happens with many organic polymers (Šrámek and Králová, 1981). However, it may break down in the presence of silane vapour during re-application of consolidant if the previous application has not fully cured (BRE pers. comm.).

Monomeric silanes may evaporate from a stone surface before polymerisation takes place (Clifton, 1980). Evaporation rates are faster for monomers of lower molecular weights. If vaporised monomers are condensed on other surfaces, polymerisation may take place outwith the area intended to be consolidated. Polymerisation occurs via three stages of hydrolysis, alcoholic condensation and dehydration condensation (Danehey *et al.*, 1992). Danehey *et al.* (1992) showed that the presence of calcite in a stone retards the condensation stage. In calcareous stone types (e.g. limestones and calcareous sandstones) this may allow significant quantities of silane to evaporate before polymerisation can occur. Bonding of silane polymers to calcite is much weaker than to silica (Charola *et al.*, 1984a) where surface hydroxyl groups can form bonds between the polymer and the substrate.

Brethane (Price, 1981), a stone preservative developed by the Building Research Establishment is an alkyltrialkoxysilane (see below). Brethane has three components (including a catalyst) which are mixed immediately before use. The mixture is periodically sprayed onto dry stonework over several hours until no more can be taken up. Depth penetration is said to be several centimetres and this relatively deep penetration is achieved by the low viscosity of the mixture. The mixture remains thin for several hours after application then sets rapidly to form a gel which slowly shrinks and hardens. The development of Brethane (BRE pers. comm.), which used a catalyst rather than water to initiate the chain reaction, resulted in the conclusion that temperature control and catalyst concentration were perhaps the most important factors in consolidation. Indeed if a consolidant was applied to a dry wall with no catalyst, in very cold weather, the treatment might all evaporate. Also the size of the containers which are bought with Brethane were the result of research into temperature effects and designed uniquely for Brethane. Essentially, on mixing Brethane, an exothermic reaction produces a certain temperature change. The rate of fall in temperature is controlled by the volume and heat capacity of the controlled mix size. The level of pre-polymerisation is highly temperature controlled. If the volume of Brethane is bigger than as designed, the extra heat retention sets the whole mix. If only a small amount of consolidant is mixed, it cools quickly and there is insufficient pre-polymerisation. The controlled level of pre-polyermisation is a key part of Brethane design as it makes the Brethane mix partially 'oligomeric'. More oligomeric mixes increase the pore lining characteristics of the treatment, as it matches the effects of a 'resin', rather than a 'silica gel'. The presence of salts (sodium chloride) in a stone can interfere with catalysis of setting. Brethane has been tested in situ on both sandstones and limestones. In laboratory tests Brethane was found to double the tensile strength of fresh Locharbriggs sandstone. Secondary treatments with Brethane can cause swelling and short term darkening of stone. Excess Brethane remaining on the surface can give a glossy appearance. In long term monitoring trials of Brethane (Butlin *et al.*, 1995) over up to 8 to 16 years at 10 sites in the UK (both limestone and sandstone) Brethane treated areas generally suffered less biological growth, decay and water absorption than similar untreated areas although the degree of efficacy declines over time. Most weathering of Brethane was in the outer 1-2 mm. Better results were obtained on limestone than on sandstone. No detrimental effects (in terms of decay rate) were noted at any site.

Tetraalkoxysilanes

Tetraalkoxysilanes (Figure 3(a)) have four functional groups with respect to polymerisation although in practice not all these groups will form cross-links (Horie, 1987). Tetraethoxysilane (also known, in its partially polymerised form, as ethyl silicate or as tetraethyl silicate) has been most used in stone consolidation. It hydrolyses in the presence of traces of water to form tetrahydroxysilane and ethyl alcohol. Tetrahydroxysilane is unstable and polymerises on dehydration to form silica gel. Silica is deposited as water is lost slowly from the gel (Ashurst and Dimes, 1990; Clifton, 1980). Having no attached alkyl groups this consolidant has no water repellent effect.

Alkyl trialkoxysilanes

Alkyl trialkoxysilanes have three functional groups with respect to polymerisation. The simplest form of alkyl trialkoxysilane is methyl trimethoxysilane (Figure 3(b)). Longer chained alkoxy groups may be attached. The larger the group, the slower the rate of hydrolysis (Lewin and Wheeler, 1985). These compounds polymerise in the same way as tetraalkoxysilanes. They differ from tetraalkoxysilanes in that an alkyl group remains attached to each monomer and this reduces the degree of cross-linking. This reduces the potential degree of consolidation but gives some water repellency (the degree of water repellency depends on the nature of the attached group) (Ashurst and Dimes, 1990; Šrámek, 1993).

Sometimes silanes are described as silicon esters. Silicon esters are partially polymerised alkoxysilanes which still have some ester groups attached (Clifton, 1980).

Polysiloxanes

These compounds contain Si–O–Si bonds (Figure 3(c)) and form by polymerisation or partial polymerisation (i.e. oligomers) of silanes. Polysiloxanes have a higher molecular weight than silanes and this can be useful in reducing the degree of evaporation that may take place before polymerisation is complete. They are soluble in organic solvents such as xylene or toluene. As with silanes, alkyl and other groups (e.g. phenyls) may be attached. The presence of a carbon ring structure such as phenyl (C_6H_5-) gives the polymer a degree of flexibility in addition to water repellency (Ashurst and Dimes, 1990).

Silicon hydrides

Silicon hydrides theoretically capable of forming network polymers would include the forms $RSiH_3$ and SiH_4. They have been little used since they are gases and volatile liquids, are difficult to use and transport and their use involves the formation of hydrogen gas (Lewin and Wheeler, 1985).

Halogen bearing silanes

Fluorosilanes theoretically capable of forming network polymers have the basic form $RSiF_3$ and SiF_4. Chlorosilanes have the same basic form but contain chlorine in place of fluorine. They generate damaging acids during hydrolysis and have been found to be too toxic, volatile and reactive for use in stone conservation (Lewin and Wheeler, 1985).

Silane-based consolidants, due to their low viscosity, are generally able to penetrate relatively deeply into the stone before polymerisation occurs (Charola *et al.*, 1984a; Clifton, 1980) although results may vary dependent on the stone type and the method of application. Some investigators have found penetrations of up to 70 to 80 mm (Rossi-Manaresi, 1981; Snethlage *et al.*, 1989) although results vary depending on the stone type, the silane used and the conditions under which it is applied. Other investigators have found penetration to be less than 10 mm (Caro Calatayud, *et al.*, 1992; Caselli and Kagi, 1995; Pavia Santamaria *et al.*, 1992). Penetration into the stone may be improved in a number of ways including the use of slow evaporating solvents, surface treatment or simply covering the surface with an impermeable membrane (Horie, 1987). It should be noted that if a surface is re-treated before polymerisation is complete it can result in swelling and disruption of the treated area (Ashurst and Dimes, 1990; Hanna, 1984). The presence of salts in stone may reduce the adhesion of silanes (Biscontin *et al.*, 1993).

The film-forming properties of polymers can be investigated by scanning electron microscope (SEM) studies. Charola *et al.* (1984b) and De Witte *et al.* (1985) found that the properties of films formed on limestones varied depending on the characteristics of the monomer or oligomer used. Tetraethoxysilane (De Witte *et al.*, 1985) and MTMOS (Charola *et al.*, 1984b) tended to form a network of strands while a partially pre-polymerised MTMOS solution gave a more even, relatively heavy coating unless the amount of solvent used was larger (Charola *et al.*, 1984b) in which case the coating was less uniform and thinner. De Witte *et al.* (1985) suggest that the spongy network of strands which formed with tetraethoxysilane was due to the inability of the polymer to bond with the substrate, instead it tended to bond to itself forming discrete masses. The polymers coated limestone mineral grains but did not bond to them. On sandstones the film formation could, of course, be completely different due to the different bonding characteristics of the substrate.

Many investigators have reported substantial increases in the strength of sandstones treated with silanes. This included increases in compressive strength (Caselli and Kagi, 1995; Ciabach and Lukaszewicz, 1993; Saleh *et al.*, 1992; Zinsmeister *et al.*, 1988), tensile strength (Price, 1981; Saleh *et al.*, 1992), flexural strength (Snethlage *et al.*, 1989), hardness (Caselli. and Kagi, 1995) and modulus of rupture (Wheeler *et al.*, 1992; Zinsmeister *et al.*, 1988). The abrasion resistance of the stone may also be substantially improved (De Witte and Bos, 1992; Zinsmeister *et al.*, 1988).

Some investigators have noticed colour changes on application of silanes which mainly involve darkening of the stone surface (Caro Calatayud *et al.*, 1992; Clifton, 1984; Lukaszewicz *et al.*, 1995; Pavia Santamaria *et al.*, 1992; Price, 1981; Rossi-Manaresi, 1976b; Saleh *et al.*, 1992; Rossi-Manaresi *et al.*, 1995; Wheeler *et al.*, 1992) although others have not (Auras, 1993; Zinsmeister *et al.*, 1988). Lukaszewicz *et al.* (1995) suggest that the colour changes are caused by the presence of clay minerals in the stone. Some authors (Lukaszewicz *et al.*, 1995; Rossi-Manaresi, 1981; Rossi-Manaresi *et al.*, 1995; Wheeler *et al.*, 1992) have also noticed white deposits on treated stone. Lukaszewicz *et al.* (1995) detected white deposits which they identified as gypsum and silica on a sandstone surface one year after treatment with a silane.

Investigators have found that the performance of silane compounds varied depending on sandstone type (Clifton, 1980). Clifton (1980) notes a number of instances where authors have reported different results. Some found some loss in porosity (Ciabach and Lukaszewicz, 1993; De Witte and Bos, 1992; Snethlage and Klemm, 1978; Zinsmeister *et al.*, 1988), but others found little effect on porosity (Arnold *et al.*, 1976; Auras, 1993; Bosch, 1972; Moncrieff, 1976; Price, 1975).

Treatment with silanes has the potential to alter the vulnerability of sandstones to damage by salt crystallisation or freeze-thaw through changes in pore size distribution. As mentioned above, some investigators have found significant changes in the porosity of treated stones. With regard to vulnerability to salt and frost decay processes, some investigators have found no changes (De Witte and Bos, 1992), others have found increased vulnerability (Caro Calatayud *et al.*, 1992; De Witte and Bos, 1992; Pavia Santamaria *et al.*, 1992; Villegas and Vale, 1992) and others have found decreased vulnerability (Villegas and Vale, 1992). It is likely that changes in the vulnerability of sandstone to these forms of decay are controlled by the specific pore size distribution in the stone and by the conditions under which the consolidant is introduced into the stone. It is possible that the outcome of consolidation in relation to these factors would not be easily predictable.

Changes in water absorption and evaporation rates are affected by changes in the porosity of the stone as well as by any water repellent properties inherent to the material applied. This can affect the rate of decay of the stone. Any reduction in the amount of water which can gain access to the interior of the stone might be expected to reduce the decay rate since water is involved in many of the decay processes. A number of investigators have found that some silanes (especially those which have water repellent properties) have substantially reduced the water absorption of sandstones (Angel Bello *et al.*, 1992; Caselli and Kagi, 1995; Ciabach and Lukaszewicz, 1993; De Witte and Bos, 1992; Hosek and Šrámek, 1992; Saleh *et al.*, 1992; Sasse *et al.*, 1993; Valdeón *et al.*, 1992; Villegas and Vale, 1992; Zinsmeister *et al.*, 1988) although results may be highly variable (Snethlage *et al.*, 1989). Some authors calculate figures for the "protective efficacy" of a treatment (see Section 2.3.2) based on the changes in moisture absorption which are measured before and after treatment (Appolonia *et al.*, 1995). However, it is not only the amount of water which gains access to the interior of a stone which controls the decay rate but also, and perhaps more importantly, the length of time over which the stone remains damp. Treatments which reduce the rate of moisture evaporation from the stone surface may therefore increase the rate of decay and a number of investigators have found substantial reductions in the rate of moisture evaporation from treated stones (Caselli and Kagi, 1995; De Witte and Bos, 1992; Sasse *et al.*, 1993; Valdeón *et al.*, 1992) although again results may vary (De Witte and Bos, 1992).

The interaction of moisture movement and pollutants in a stone can also be of great importance in relation to decay processes. It is likely that if the stone surface has a water repellent coating, moisture evaporation will be forced to take place inside the body of the stone and may lead to deposition of potentially damaging salts at the boundary between the treated and the untreated stone. Even if the surface treatment prevents access into the stone of pollutants in rain water, if the stone has previously been exposed for any length of time, pollutants will already exist in the stone. Pollutants may also gain access to a treated stone through water percolation along cracks at mortar joints, from internal movement between blocks, by rising damp from ground water and through absorption in the gaseous phase from the atmosphere. Indeed some investigators (De Witte and Bos, 1992) have found that treated sandstones were more vulnerable to decay caused by deposition of pollutants from the gaseous phase than untreated sandstones.

Long term results obtained from using silanes vary widely. Clarke and Ashurst (1972) found that where these substances had been used on sandstones, in almost 80% of cases the rate of stone decay was unchanged and there was no significant reduction in the rate of decay in any case relative to control panels. Although Ciabach and Lukaszewicz (1993) and Caselli and Kagi (1995) have found treatments to be stable for at least 1 or 2 years, Rossi-Manaresi *et al.* (1995) and Snethlage *et al.* (1989) found the preservation effects to be relatively short lasting (i.e. less than 20 years). After 10-15 years Snethlage *et al.* (1989) found there to have been almost total loss of hydrophobisation.

Effects of attaching different functional groups to silanes

The most basic form of silane is a tetraalkoxysilane where all four groups attached to the central silicon atom are capable of forming cross-links with other silane molecules. With trialkoxysilanes and dialkoxysilanes, only three or two (respectively) groups attached to the silicon are capable of forming bonds with other silane molecules. The other groups are commonly methyl or ethyl groups which are used to confer some water repellent characteristics to the consolidant. However, other groups have been tested. Among these are:-

hydrogen: hydrogenmethoxysilane (Hosek and Šrámek, 1992). This compound is highly toxic (Lewin and Wheeler, 1985)

butyl: methyltributoxysilane or dimethyldibutoxysilane (Šrámek and Králová, 1981)

phenyl: methylphenylsiloxane (Rossi-Manaresi, 1981; Rossi-Manaresi *et al.*, 1995; Santamaria *et al.*, 1995)

acrylic: *y*-methacryloxypropyl-trimethoxysilane (Angel Bello *et al.*, 1992; Šrámek and Králová, 1981; Villegas and Vale, 1992)

amine: e.g. *y*-aminopropyl-trimethoxysilane or

N-2-aminoethyl-3-aminopropyl-trimethoxysilane (Wheeler *et al.*, 1992)

polyurethane: organosilicone modified polyurethane (Sasse *et al.*, 1993)

epoxy: *y*-glycidoxypropyl-trimethoxysilane (Wheeler *et al.*, 1992)

For most of these compounds there were no outstanding differences in performance from other “more conventional” silanes although hydrogenmethylmethoxysilanes (Hosek and Šrámek, 1992) were better able to bond to clays through reaction between the hydrogen in the silane and hydroxy groups on the surfaces of clays. Depth of penetration varied from a few millimetres up to 7 cm. Some significant increases in strength were observed. In some cases (amines and epoxy groups) darkening of the surface was noted. Water absorption was reduced in some cases. The only case in which a distinct disadvantage was noted in the performance of any of these compounds was with hydrogenmethylsiloxane (Hosek and Šrámek, 1992) which violently released hydrogen gas and could be damaging to a fragile stone. In the absence of direct comparisons between different silanes it is not possible to draw any distinction between the performance of these more “exotic” and “more conventional” silanes.

2.2.3.2 Organic-based materials

Organic consolidants may be applied to the stone as monomers which then polymerise inside the stone or as oligomers or polymers dissolved in appropriate solvents. Organic consolidants are good at adhering to substrates and, due to their plastic behaviour, they are generally good at taking up dimensional changes in a stone (e.g.

thermal expansion and contraction) (Palma Dias, 1992). Many organic polymers are however vulnerable to degradation when exposed to heat or ultra-violet light (Clifton, 1980; Palma Dias, 1992).

Acrylic consolidants

Acrylic resins are generally derived either from acrylates or from methacrylates (Figure 3(d)) (Horie, 1987). They may be thermoplastic or thermosetting depending on whether or not they are cross-linked. Cross-linking can be achieved by the use of a suitable catalyst such as benzoyl peroxide. Polymerisation of methyl methacrylate can be initiated by the use of heating with chemical promoters and initiators and by gamma radiation (Clifton, 1980). Thermoplastic polymers are generally soluble in an appropriate organic solvent (e.g. trichloroethylene). The hardness of acrylic polymers depends on the size of the alkyl group, with the polymer softening, the larger the group, so that butylmethacrylate (Srámek and Králová, 1981) is quite soft (Ashurst and Dimes, 1990). Polymerisation is inhibited by the presence of oxygen, which causes the formation of methyl methacrylate peroxides (Koblischek, 1985; Kwiatkowski, 1985).

Acrylics which have been tested as sandstone consolidants include methylacrylate (Angel Bello *et al.*, 1992; Caro Calatayud *et al.*, 1992; Horie, 1987; Pavia Santamaria et al., 1992; Petersen *et al.*, 1992; Saleh *et al.*, 1992; Villegas and Vale, 1992; Wheeler *et al.*, 1992), methyl methacrylate (Clifton, 1984; Šrámek and Králová, 1981), ethyl methacrylate (Angel Bello *et al.*, 1992; Caro Calatayud *et al.*, 1992; Horie, 1987; Pavia Santamaria *et al.*, 1992; Petersen *et al.*, 1992; Saleh *et al.*, 1992; Villegas and Vale, 1992; Wheeler *et al.*, 1992) and butyl methacrylate (Šrámek and Králová, 1981).

Horie (1987) and Koblischek (1985) note that polymethyl methacrylate (PMMA, poly[1-(methoxycarbonyl)-1-methyl ethylene]) is very stable to degradation by heating, oxygenation and ultra-violet radiation and will not yellow with age (since it does not absorb UV light (Gauri *et al.*, 1976)), but polyalkylmethacrylates with larger alkyl groups and all polyalkyl acrylates are less stable and will yellow on exposure to ultra-violet light. Šrámek and Králová (1981) note that butyl methacrylate (PBMA, poly[1-(butoxycarbonyl)-1-methyl ethylene]) is unstable to UV radiation. However, Šrámek and Králová (1981) found that PMMA was fairly unstable to UV radiation when used as a stone consolidant. This apparent contradiction with the results of Horie (1987) and Koblischek (1985) occurs due to the presence of impurities in the PMMA which do absorb light at UV wavelengths (Gauri *et al.*, 1976). Koblischek (1985) notes that PMMA is only non-yellowing where it is polymerised by heat or UV, or where the proportions of reactants are precisely balanced.

Little data was available in the literature regarding colour changes caused by application of acrylic polymers to stone although Clifton (1984) and Pavia Santamaria *et al.* (1992) noted darkening of the surface on application of methyl methacrylate and polymethylacrylate (PMA, poly[1-(methoxycarbonyl)-ethylene]) respectively. Clifton (1984) however noted no colour change on application of another acrylic (composition unknown) and Saleh *et al.* (1992) found little colour change on application of a mixture of acrylic (methylacrylate and ethylmethacrylate) and silane polymers.

It is difficult to achieve good penetration using these polymers if they are carried in a solvent as they tend to be drawn back to the surface as the solvent evaporates (Lewin and Papadimitriou, 1981). Effects differ depending on the solvent used. Some solvents may penetrate the stone but fail to carry the consolidant with them. Penetration may be inhibited by the presence of moisture in a stone as acrylics are immiscible with water (Saleh *et al.*, 1992). With respect to impregnation depth, Lewin and Papadimitriou (1981) suggest that the order of effectiveness of a number of solvents for use with polymethyl methacrylate was CH_2Cl (methylene chloride) > $CHCl_3$ (chloroform) > $C_6H_5CH_3$ (toluene) > CCl_4/C_2H_5OH (1:1, carbon tetrachloride + ethanol (95%)). While using the methylene chloride solvent Lewin and Papadimitriou (1981) were able to achieve complete penetration of 5 cm limestone cubes, the carbon tetrachloride-ethanol mixture achieved no significant penetration. Results were found to be strongly dependent on polymer concentration and solvent type. No generalisation could be made.

Better results may be achieved if polymerisation takes place after penetration of the monomer (Ashurst and Dimes, 1990). Penetration achieved varies from "very good" (Clifton; 1984) to under 5 mm (Pavia Santamaria *et al.*, 1992) to "poor" (Saleh *et al.*, 1992).

Acrylics can substantially increase the modulus of rupture (Wheeler et al., 1992) and compressive strength (Saleh *et al.*, 1992) of sandstones either where the acrylic is used alone and where it is used in combination with silanes.

No data have been found in the literature regarding the effects of acrylic resins alone on sandstone porosity or water evaporation rates although some investigators (Angel Bello *et al.*, 1992; Saleh *et al.*, 1992; Villegas and

Vale, 1992) have found substantial reductions in water absorption. In some tests of mixed acrylics and silanes Saleh *et al.* (1992) found some near surface blockage but with another mixture they found no effects on porosity although in both cases water absorption was reduced.

In tests of acrylic polymers a number of investigators (Pavia Santamaria *et al.*, 1992; Villegas and Vale, 1992) have found that they increased the susceptibility of sandstone to decay through salt crystallisation. Petersen *et al.* (1993) have found that acrylics are vulnerable to microbial attack and Šrámek and Králová (1981) have found them to be vulnerable to degradation by SO_2. Horie (1987) notes that acrylics degrade slowly over time. There is little data available about the longer term effectiveness of acrylic consolidants although Rossi-Manaresi *et al.* (1995) found that a mixture of acrylic and silane polymers were still effective, although altered, after 20 years.

Vinyl consolidants

Vinyl consolidants include polyvinylchloride (PVC, poly(1-chloroethylene)) and polyvinylacetate (PVA, poly(1-acetoxyethylene)) (Figure 3(e)). These have generally been unsuccessful as stone consolidants since they tend to give the surface a glossy appearance and it is difficult to achieve good penetration. In addition, it is possible that with the use of PVC or similar compounds release of chlorine could be damaging to the stone (Clifton, 1980). PVC is very unstable to light and heat, degrading and releasing HCl. Polyvinylacetate is stable to UV and degrades only very slowly although it tends to pick up dirt and displays cold flow over long periods. It absorbs water, turning white and opaque but reverting to a clear state on drying (Horie, 1987).

Epoxies

Epoxy resins are formed by a two-stage reaction (Figure 3(f)). In the first stage a low molecular weight polymer is formed (e.g. with a bisphenol and epichorohydrin) with reactive epoxy groups at each end. In the second stage a cross-linking agent is added. This is generally a polyfunctional amine.

Epoxy resins are prone to yellowing or formation of a white powdery surface due to oxidation or UV exposure (Clifton, 1980; Horie, 1987; Koblischek, 1985; Šrámek and Králová, 1981). Investigators have found darkening of the sandstone on application of epoxies (Clifton, 1984; Rossi-Manaresi, 1981) and Saleh et al. (1992) noted the presence of a white deposit on the sandstone surface.

Although little information has been found in the literature regarding the effects of epoxies on sandstone strength, epoxy resins can increase the modulus of rupture of sandstone (Wheeler *et al.*, 1992). However, available evidence suggests that it may be difficult to achieve adequate penetration of the stone (Ashurst and Dimes, 1990) due to the high viscosity and hydrophobic characteristics of many epoxy resins. Measured penetrations may be only up to 1 cm (Clifton, 1984; Rossi-Manaresi, 1981). However, Cavaletti *et al.* (1985) describe the testing of an aliphatic epoxy resin of relatively low viscosity with good UV stability. This epoxy also was also miscible with water (allowing penetration of humid stone) had good mechanical properties and was reasonably resistant to chemical attack (by O_2, CO_2 and SO_2). Some aliphatic epoxies have low chemical resistance and may be highly toxic.

No information has been found in the literature regarding the effects of epoxy consolidants on sandstone porosity or water evaporation rates although Sasse *et al.* (1993) found some reduction in water absorption. Epoxies can be degraded by SO_2 (Šrámek and Králová, 1981).

Epoxy resins have generally been found to be impractical for use in the consolidation of sandstone due to their low penetration.

Polyurethane

Polyurethanes (Figure 3(g)) are prepared from reaction of an excess of isocyanates with alcohols (diols). Isocyanates are highly toxic. The urethane prepolymer reacts with moisture giving off urea and CO_2 to form polyurethane (Auras, 1993; Horie, 1987; Littmann *et al.*, 1993). The composition of the prepolymer may be altered to change the chemical and physical properties of the polyurethane. Curing velocity is controlled by the reactivity of the isocyanate compound and elastic properties are controlled mainly by the alcohol component (Littmann *et al.*, 1993). Polyurethanes are introduced into stone in solvents and deposited as the solvent evaporates (Auras, 1993). Polyurethanes are vulnerable to decay caused by exposure to heat or light and may therefore include stabilisers (Horie, 1987; Koblischek, 1985).

Polyurethanes can increase the strength of a stone (Wheeler *et al.*, 1992). They have been found to increase the modulus of rupture (Wheeler *et al.*, 1993) and the bending strength (Littmann *et al.*, 1993) of sandstones although this can leave the stone very brittle and may create a hard external shell (Littmann *et al.*, 1993). Polyurethanes can penetrate sandstone relatively deeply, up to 6-12 cm in some cases (Auras, 1993; Littmann *et al.*, 1993), although results can vary and some investigators have found penetration to be poor (Clifton, 1984; Rossi-Manaresi, 1981; Valdeón *et al.*, 1992). Penetration in limestones is generally poor (De Witte *et al.*, 1985). The effects of polyurethanes on stone colour have been found to be quite variable. Some investigators found no effect (Auras, 1993), others found slight effects (Valdeón *et al.*, 1992) and others found darkening of the surface (Clifton, 1984). Auras (1993) found no effects on porosity on application of a polyurethane to sandstone although other authors have found reduction in water absorption (Littmann *et al.*, 1993; Rossi-Manaresi, 1981; Valdeón *et al.*, 1992) and in water evaporation rates (Littmann *et al.*, 1993; Valdeón *et al.*, 1992). Polyurethanes have been found to increase the vulnerability of sandstone to decay caused by salts leading to spalling of the surface (Valdeón *et al.*, 1992). Fluorinated polyurethanes (Guidetti *et al.*, 1992) are chemically very stable and hydrorepellent. They can be applied in water emulsions and are 90-95% reversible using methyl alcohol and Freon 113. They cause relatively little colour change in stone.

Polyesters

These are not resistant to UV radiation (Šrámek and Králová, 1981) to SO_2 (Šrámek and Králová, 1981) or to alkalis (Koblischek, 1985). Their long term performance is poor and they have not been found to be useful in stone conservation (Koblischek, 1985).

Perfluoropolyethers

Perfluoropolyethers (Figure 3(h)) are very stable to UV (Frediani *et al.*, 1982; Piacenti *et al.*, 1985) and have the advantage, in conservation terms, of being theoretically reversible through their solubility in fluorinated solvents (Chiavarini *et al.*, 1993; Horie, 1987). These products remain mobile within a stone and their performance therefore gradually declines over time. Degree of mobility is affected by the polarity and size of the functional groups (Chiavarini *et al.*, 1993; Piacenti *et al.*, 1985; Piacenti *et al.*, 1993) and the porosity of the stone, the decline in protective efficacy being slower with some functional groups and in less porous stone (Piacenti *et al.*, 1993). These products generally work best in stone types of lower porosity (Appolonia *et al.*, 1995). The use of a polyurethane co-polymer (Chiavarini *et al.*, 1993) provides a functional group which is capable of physically bonding with the stone and results in a much more long lasting water repellent effect.

Perfluoropolyethers are generally used as water repellents as they have little or no cohesive effect (Ashurst and Dimes, 1990; Chiavarini *et al.*, 1993; Manganelli del Fa' *et al.*, 1981; Tiano *et al.*, 1985) unless the polymer contains polar functional groups capable of bonding to the stone (Chiavarini *et al.*, 1993; Piacenti *et al.*, 1985, 1992, 1993a). Piacenti *et al.*, (1993a) have reported good results using an isobutylamide of a perfluoropolyetheric monocarboxylic acid. Where perfluoropolyethers remain mobile in the stone their depth of penetration changes over time although penetration of perfluoropolyethers is often low (e.g. a few millimetres) in sandstones (Tiano *et al.*, 1985). Tiano *et al.* (1985) found a moderate reduction in porosity following perfluoropolyether application to sandstone. Effects on water absorption have varied from little effect (Angel Bello *et al.*, 1992; Frediani *et al.*, 1982) to moderate (Frediani *et al.*, 1982; Manganelli del Fa' *et al.*, 1981; Tiano *et al.*, 1985) or substantial reductions (Rossi-Manaresi, 1981). Little effect has been found on water evaporation rates (Frediani *et al.*, 1982; Manganelli del Fa' *et al.*, 1981).

Fluorinated elastomers

Results of the treatment of limestone with fluorinated elastomers are described by Piacenti *et al.* (1993b). The material used was a hexafluoropropene-vinylidene fluoride copolymer. It was applied in acetone and in water emulsion. The product greatly reduced water absorption and vapour permeability was reduced by up to 25%. In abrasion tests, weight losses were reduced by up to 85% compared to controls. The product in acetone or butyl acetate solution gave the greatest reduction in water absorption, vapour permeability and abrasion weight loss. Under SEM examination differences were noted in the dispersion of the material in acetone solvent and in water emulsion. In water emulsion the product formed small spheres in pores. In acetone solution the product formed a network of filaments.

2.2.3.3 Inorganic treatments

Fluosilicates

Fluosilicates of magnesium, zinc and aluminium have been tested as stone consolidants (Dukes, 1972). Fluosilicate treatment of limestones resulted in formation of calcium fluoride deposits on calcite surfaces (De Witte *et al.*, 1985). These deposits were not attached to calcite grains (SEM observations) but were deposited interstitially. Acids are produced which will attack calcareous stones resulting in the formation of a hardened surface layer through deposition of calcium fluorides (Rossi-Manaresi, 1981). In sandstones, Roselli and Rosati (1992) note that highly hygroscopic amorphous silica has been deposited. Roselli and Rosati (1992) report that a good quality sandstone, consolidated by immersion in fluosilicates when newly cut, was still in excellent condition fifty years later; by contrast, a similarly consolidated poor quality sandstone was badly decayed. It was not possible to relate either the good condition of one, nor the poor condition of the other to the effects of the consolidant. Roselli and Rosati (1992) note several instances in which fluosilicate consolidation was suspected to be responsible for exfoliation and accelerated deterioration of treated sandstones although, due to the uncontrolled methods used, no conclusive evidence was available. Fluosilicates can also cause colour changes to sandstones (Roselli and Rosati, 1992) and Rossi-Doria *et al.* (1978) note that they have poor penetration and can give rise to soluble salts.

Hydrofluorosilicic acid has been used as a consolidant of sandstones. It must not be used on calcareous stones as the acid will react with the calcium carbonate. On sandstones, hydrofluorosilicic acid treatment has been found to produce only a superficial consolidated layer at the surface. Fluorosilicates have not been found to be successful as consolidants (Clifton, 1980; Rossi-Manaresi, 1981).

Barium-hydroxide

Treatments involving barium hydroxide have been used for the consolidation of decayed limestone. Treatment with barium hydroxide, in addition to the formation of barium carbonate (witherite), also results in the transformation of calcium sulphate into the relatively insoluble barium sulphate (Lewin and Baer, 1974). Treatments in the past have followed the barium compound with a second acid solution to form an insoluble precipitate with the barium. Silicic, fluosilicic, carbonic, sulphuric, chromic and phosphoric acids have been used (Lewin and Baer, 1974). Disadvantages of these treatments include colour or textural changes and the short term nature of any consolidation effects.

An alternative treatment method developed by Lewin (1966, 1971) (Lewin and Baer, 1974) resulted in consolidation of limestones lasting at least seven years and (with some exceptions) producing little colour change. In coloured limestones, the white colour of the precipitate may be noticeable. For small objects the treatment involved immersion for one day in a hot, concentrated solution of $Ba(OH)_2$ containing 10% urea. For objects which cannot be immersed a glycerine-water solvent mixture is used, the glycerine (and covering) being used to prevent rapid drying of the treated surface since the treated area should remain wet for a period of three weeks (Lewin and Baer, 1974). Where the treated stone is kept wet for long enough, barium and calcium carbonates can form a solid solution series and the mechanism of consolidation results in formation of barium calcium carbonate of increasing barium content away from the original calcium carbonate crystal (Lewin and Baer, 1974).

Limewater

Lime has been used as a consolidant for limestones (Price, 1984). One technique, described by Price (1984) consisted of the application of a poultice (20-30 mm thick) of hot, freshly slaked lime to pre-wetted stone. The paste is covered with sacking and polythene sheeting for two to three weeks and is wetted daily to prevent drying out. When the poultice is removed, the stone is sprayed with water and gently brushed to remove any remaining debris. Limewater is then flooded onto the stone about 40 times over several days. Price (1984) noted that best results are achieved where the limewater is as cold as possible. He suggests that this may be because calcium hydroxide is precipitated as the solution warms up on application to the stone (calcium hydroxide being more soluble at lower temperatures). A final shelter coat of lime, sand and stone dust is then applied. Lime is converted into calcium carbonate by carbonation in contact with the atmosphere. Results have varied and while some authors report good outcomes others have found results to be poor.

In the laboratory Price (1984) attempted consolidation of crushed limestone by soaking the crushed stone in limewater and drying over several days. The cycle of soaking and drying was repeated 30 times. No noticeable consolidation was achieved. Price (1984) suggested several explanations for this. Firstly, that the experimental situation was not a good simulation of what happened in situ where, for instance, the stonework might remain damp for longer periods than in the laboratory. Secondly, that perhaps consolidation in situ was achieved only on a thin surface layer whereas, in the laboratory, consolidation in depth was attempted. Thirdly, he suggested that consolidation in situ might be due to factors other than the lime poultice and limewater. For instance, consolidation might be achieved by solution and redeposition of calcium sulphate rather than calcium carbonate.

2.2.3.4 Mixtures of consolidants

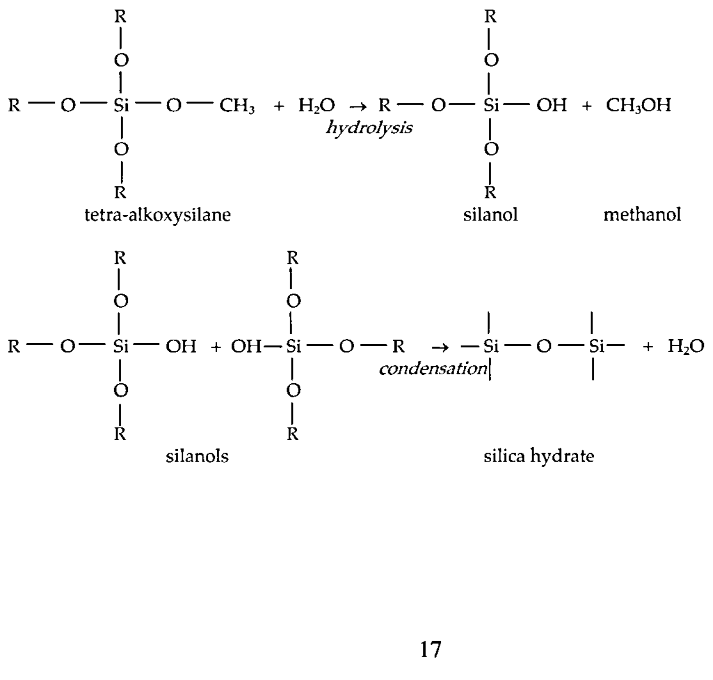
Some investigators have tested mixtures of consolidants of different types. Most commonly this has been an acrylic resin along with, or followed by, a silane. Saleh *et al.* (1992) and Wheeler *et al.* (1992) obtained good results for consolidation of sandstone using a mixture of an acrylic resin (Paraloid B-72) and various silanes with good strength increases, little colour change and substantially decreased water absorption. Hanna (1984) also notes that mixing an acrylic resin with a silane allows deeper penetration of the acrylic than would otherwise be possible. Rossi-Manaresi and Tucci (1984) also noted good results (no colour change, good water repellency and consolidation) using a mixture of Paraloid-B72, Dri Film 104 and limewater on a calcareous sandstone. Testing a mixture of acrylic resin (Paraloid B-72) and methylpolysiloxane (HEY D'I M.S. Siloxane) however, Saleh *et al.* (1992) found the depth of penetration to be poor and there was some near surface blockage of porosity. Using an acrylic resin (Paraloid B-72) and a methyltrimethoxysilane (Silicone Dri Film 104) Appolonia *et al.* (1995), Rossi-Manaresi (1981) and Rossi-Manaresi *et al.* (1995) also found depth of penetration to be poor although the consolidant was thought still to be effective after 20 years (Rossi-Manaresi *et al.*, 1995). Using an epoxy resin followed by a silane (tetra-ethyl-orthosilicate), Rossi-Manaresi (1981) obtained moderate penetration (0.5-1 cm) and good preservation but observed bad white discoloration. Caselli and Kagi (1995) used two silanes (Wacker OH and Wacker 280). Penetration was poor although hardness and strength were substantially increased and water absorption reduced with only a moderate fall in the water evaporation rate.

From the information available in the literature there was no indication of any advantages to be gained in using any of these mixed treatments over other single treatments although comparisons are difficult to make since so many different factors and testing methods are involved.

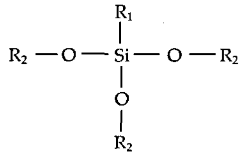
2.2.3.5 Other materials

Many other materials have been used as consolidants. Soluble alkali silicates and dispersions of silica in sodium hydroxide have been used to deposit silica in stone. However, in order to precipitate silica, alkali silicates must react with acids (e.g. hydrochloric acid) forming soluble salts. The introduction of sodium hydroxide to a stone will also result in the formation of soluble salts. Both these methods of consolidation can be extremely damaging to a stone (Clifton, 1980).

(a) Polymerisation of tetra-alkoxysilane [where R is an alkyl group, e.g. $-CH_3$, $-C_2H_5$, etc.].

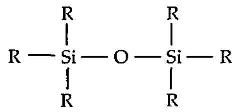


(b) Alkyl-trialkoxy-silane [where R_1 and R_2 are alkyl groups, e.g. $-CH_3$, $-C_2H_5$, etc.]. The polymerisation proceeds similarly to that shown in (a).



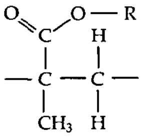
$$R_2-O-\overset{\displaystyle R_1}{\underset{\displaystyle \underset{\displaystyle R_2}{O}}{Si}}-O-R_2$$

(c) Example of a siloxane [where R are functional groups, e.g. $-CH_3$, $-C_2H_5$, phenyl, etc.]. The polymerisation proceeds similarly to that shown in (a).

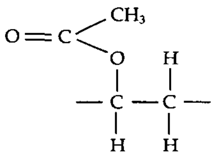


$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-O-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-R$$

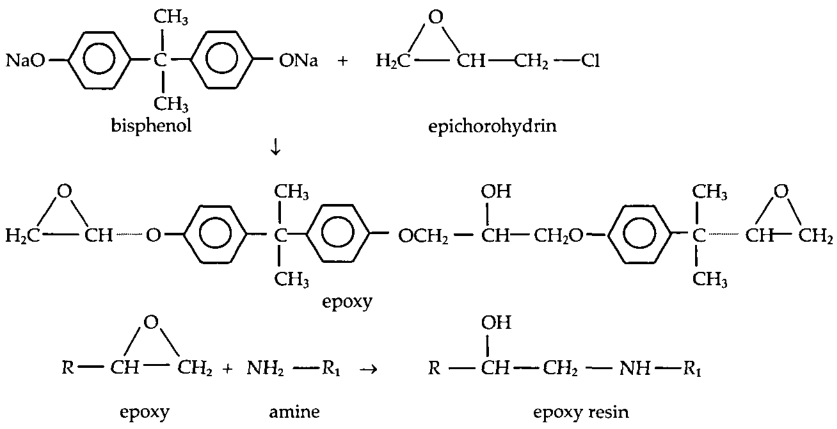
(d) Polyalkylmethacylate [where R is an alkyl group, e.g. $-CH_3$, $-C_2H_5$, etc.].



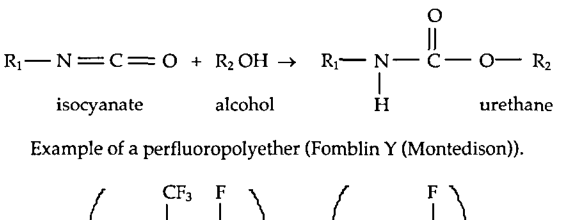
(e) Monomer unit of polyvinylacetate.



(f) Example of formation an epoxy resin (R and R_1 are groups of various compositions) (Allinger, 1980; Horie, 1987).

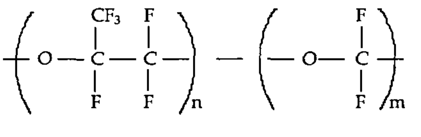


(g) Urethane produced from isocyanate and alcohol (R_1 and R_2 are groups of various composition).



$$R_1-N=C=O + R_2OH \rightarrow R_1-\underset{\displaystyle H}{N}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R_2$$

(h) Example of a perfluoropolyether (Fomblin Y (Montedison)).



$$\left(O-\overset{\displaystyle CF_3}{\underset{\displaystyle F}{C}}-\overset{\displaystyle F}{\underset{\displaystyle F}{C}}\right)_n-\left(O-\overset{\displaystyle F}{\underset{\displaystyle F}{C}}\right)_m$$

Figure 3 Structures of some commonly used stone consolidants and water repellents.

2.2.4 Method of application

For any given consolidant or water repellent treatment, the method of application may be very important with respect to the depth of penetration of the treatment. Application methods include: brushing, spraying, dropwise application, capillary absorption, vacuum impregnation, pressure impregnation and total immersion.

Good penetration of stone cannot be achieved if the preservative substance polymerises too rapidly. Some systems therefore add catalysts to the monomer-solvent mixture which cause rapid, but delayed, setting or gelation at some time after application. In other systems where the monomer can be applied in the laboratory it is possible to use monomers which are polymerised by gamma radiation.

Depths of penetration achievable in laboratory settings may not necessarily be achievable in the field.

2.2.5 Vulnerability of polymers to biological decay

Polymers may be broken down by the action of microorganisms (Krumbein *et al.*, 1993; Petersen *et al.*, 1993). Indeed, Krumbein *et al.* (1993) found that some polymers not only failed to inhibit growth of microorganisms but, in some cases, the organisms used the polymers as food sources. While water repellent treatments are often thought likely to reduce microbial growth on stone through reduction of its water content, it has been shown (Leznicka, 1992) that microbial growth may actually be enhanced by some treatments. Microbial growth may be inhibited for some time by the addition of biocidal compounds to the polymer (Leznicka, 1992). Leznicka (1992) found that microbial growth was accelerated on stone samples treated with a silicone resin.

Augusta Favali *et al.* (1978) reported the presence of green alga *(Stichococcus bacillaris)* growing at 70% RH on epoxy and acryl-siliconic resins used in an attempt to prevent biological growths on stone. There was no suggestion however that the alga was causing any degradation of the polymer or stone. Nugari and Priori (1985) however, found that although two acrylic resins were not utilised as a food source by fungi, they were vulnerable to degradation, probably through attack by fungal secretions.

2.3 Testing preservative treatments for stone

Sasse *et al.* (1993) and Sasse and Honsinger (1989) suggest four main criteria by which the success of a preservative treatment may be judged. These criteria are:

- aesthetic effect,
- effectiveness and durability of protective treatment,
- building sites usability, and,
- compatibility with ecological conditions.

If a consolidant or other treatment is to be successful, it must form a strong bond with the underlying stone. In addition, the material should be able to withstand the effects of weathering and decay (including temperature and humidity changes, frost action and salt crystallisation) in a similar manner to the underlying stone. The consolidated stone should not be significantly stronger nearby sound stone or it may exacerbate decay of the surrounding stone. The consolidated area of stone must have sufficient porosity and permeability to allow passage of moisture out of the underlying stone. Ideally, the physical and chemical characteristics of the treated stone should be a close match to the untreated stone. The treatment should not be aesthetically detrimental to the stone.

2.3.1 Test beds for consolidants and water repellents

Baronio *et al.* (1992) have tested preservative treatments on sandstones using test panels constructed in an open field. Water (which can contain soluble salts, e.g. Na_2SO_4) was supplied to the subsoil to simulate capillary rise of water through a wall. Material characteristics were established under both wet and dry conditions (where there can be substantial differences in strength). Testing included petrographic analysis, compressive strength, flexural strength, splitting strength, bulk density, water absorption and absorption coefficient. Microclimatic parameters (temperature, relative humidity and pollutants) were measured as were the moisture content of the soil and the moisture and salt content of the walls. Rate of deterioration of treated and untreated wall surfaces was measured monthly. Decay could occur through the action of salt, frost, wind action and any other physical events acting on the walls. Decay rates of test samples treated with preservatives and exposed to salt crystallisation cycles were measured by measuring the difference in height of the samples over time. Baronio *et al.* (1992) found that mortar joints had an important control on moisture and salt movements within the masonry.

Bell *et al.* (1992) tested the performance of a silicone water repellent on limestone with respect to reduction in the rate of loss of soluble bicarbonate during run-off. Samples were held at an angle of 15°, fixed onto sealed containers with concrete and rubble fill to simulate the thickness of a real wall. Run-off was collected and analysed. The silicone treatment tested (Wacker 280) was found to significantly reduce the rate of loss of bicarbonate relative to untreated stones. This was attributed to the decreased residence time of water in the stone.

2.3.2 Measurement and assessment techniques

Many techniques are employed to assess the changes that take place in a stone when it has had some consolidant or water repellent agent applied to it. There are a large number of factors that may be involved in assessing the performance of any consolidant or water repellent treatment. These can include:

- physical and chemical characteristics of the protective materials,
- solvents used,
- additives (catalysts, initiators, UV protectives, etc.),
- proportions of mixes,
- curing conditions,
- colour changes on application and ageing,
- substrate mineralogy,
- substrate porosity and permeability,
- water retention and absorption characteristics of the substrate,
- load bearing requirements of structure,
- climatic influences (rainfall, humidity, temperature, incident sunlight),
- vulnerability to biodeterioration.

It is important to remember that the application of consolidants or water repellents on a building facade is likely to differ to that in a laboratory situation. Unless the laboratory method reproduces, as far as possible, conditions likely to be found in the field, results are unlikely to reflect those encountered on a building facade.

No consistent methodology has been developed for testing and consequently each investigator or laboratory uses different tests. There have been some efforts (e.g. RILEM recommendations "25 PEM" 1978: Pien, 1989) to co-ordinate testing methods between laboratories but these have so far not resulted in a unified approach to materials characterisation.

Where consolidants or water repellents with a consolidative effect are to be used it is important to test for depth of penetration since too shallow a penetration may leave a thin surface layer with different characteristics to the underlying stone and may result in spalling of the treated layer. If the surface is intended to be water repellent then changes in water absorption rate should be measured. It should be noted that many different techniques are used to measure depth penetration of consolidants and water repellents. Different techniques are likely to give different results since they measure different parameters. For example, the depth at which a water repellent material may be detected may be deeper than the level at which it is effective as a water repellent.

It is important to make sure that after treatment porosity is not too reduced as the mortar and treated stone must be able to loose moisture by evaporation to prevent trapping of moisture behind the repaired or treated zone.

The degree of expansion and contraction of the treated area on heating and cooling should be as close as possible to that of the underlying stone to avoid detachment of the mortar or treated area.

Polymers should be tested for vulnerability to degradation by UV light, by climatic conditions likely to be encountered on the building facade or by microorganisms.

The treated stone itself and the zone where it adjoins the underlying sound stone should be tested for vulnerability to decay caused by salt crystallisation or freeze-thaw action.

It is important to assess the colour and brightness of any treatment since it should be a close match for the underlying stone. The colour should match under both wet and dry surface conditions and should not alter, except to soil at a similar rate to the stone, over the life span of the treatment.

Tests of various strength parameters, including modulus of rupture and compressive and tensile strength, are probably not so important as the treated area is unlikely to be required to bear any loads. A more realistic test of the strength of a consolidant might be a test of its abrasion resistance. Tests of abrasion resistance are seldom used although they have been used by De Witte and Bos (1992) and Zinsmeister *et al.* (1988).

2.3.2.1 Method of application

The method of application of the preservative material is important as it can have a strong effect on the outcome of the treatment. In order that laboratory test results should closely compare to the results which may be expected in the field, the laboratory application method should simulate, as far as possible, the field application method. In previous studies of stone consolidants and water repellents application methods have varied widely. Some investigators brush the material onto the test surface (e.g. Saleh *et al.*, 1992) or use spray application (e.g. De Witte and Bos, 1992). These methods are likely to give results fairly comparable to those achieved in the field if the application rate and other factors (e.g. moisture content) are comparable. Some investigators use a method of capillary absorption (e.g. Sasse *et al.*, 1993) where the test specimen is immersed to a set depth (e.g. 5 mm) in the solution. Other investigators (e.g. Kotlík and Zelinger, 1978) have used vacuum impregnation, dropwise application over a number of days (Hanna, 1984) or complete immersion (Nishiura *et al.*, 1984; Rossi-Manaresi, 1976a). These last three methods are not likely to be a good simulation of the method which would be used on a building facade although they may be good for comparing results obtained on small museum specimens which can be treated under controlled laboratory conditions.

(a) Depth penetration of consolidants and water repellents

In the testing of water repellents and consolidants it is common to attempt to measure depth of penetration. It should be remembered that different measurement techniques may give very different values for depth of penetration. For instance, the depth of hydrophobic effects may be greater than the depth at which significant strengthening is measurable (Auras, 1993) but less than the depth at which the treatment is detectable.

In the method of Clifton (1984) a 140 mm diameter tube is attached by epoxy to the upper surface of a 152 mm diameter stone cube. All surfaces of the stone except the upper and lower surfaces are encased in wax. Consolidant is placed into the tube. After one hour any remaining consolidant is removed and the tube is covered to prevent evaporation. The consolidant is allowed to migrate for a further 23 hours. The specimen is then fractured or cut perpendicular to the top surface. Depth of penetration may be assessed visually if colour changes take place.

With materials which cause no visible colour change the depth of penetration may be assessed by sawing a impregnated stone sample into segments at increasing depth and measuring changes in contact angle (see below) (Littmann *et al.*, 1993).

Weber and Höhl (1988) describe the 1,5-diphenylthiocarbazone method used to measure consolidation depth.

X-ray photoelectron spectroscopy (XPS) has been used for the determination of depth penetration (Littmann *et al.*, 1993). This method measures the elemental composition of the outer surface (approx. 10 nm) of a sample and may be used in cases where the treatment has a recognisable elemental composition distinct from the underlying stone.

Depth of penetration may also be measured by IR and FTIR spectroscopy (Butlin *et al.*, 1989).

(b) Porosity and pore size distribution

Open porosity can be quantified by measuring the amount of fluid absorbed by a stone on immersion, using the following equation:

$$P_0 = [(m_1 - m_0) / V_s d_{ws}]\ 100\%$$

where,

P_0 = porosity (%)
m_0 = mass of sample before impregnation
m_1 = mass of sample treated with white spirit
V_s = sample volume
d_{ws} = density of white spirit

(Ciabach and Lukaszewicz, 1993).

While the above method can measure total interconnected porosity, it cannot give any information on pore sizes. Porosity and pore size distribution may be measured by mercury porosimetry. This method, using a range of pressures, forces mercury into a sample under vacuum. From the volume of mercury used and the pressure applied it is possible to calculate the range of pore sizes and the total interconnected porosity of the stone.

(c) Water repellency

Water repellency may be measured using the methods specified in BS 6477.

In the method as described by Henriques (1992) three separate pools of distilled water of 1±0.1 mL are placed on the test surface. The pools are examined to determine whether there has been full absorption after 10 minutes.

Water repellency can also be assessed through the measurement of contact angle (see below).

(d) Contact angle

Contact angle measurements can be used to determine the water repellency of a surface. Measurements are made, using a goniometer, of the contact angle of a water droplet of a defined volume on a horizontal surface (Sasse *et al.*, 1993). This gives an indication of the degree of water repellency of a surface. In practice, however, the contact angle is difficult to measure directly.

The difficulty of direct measurement can be avoided by calculating the contact angle from the dimensions of the droplet. For comparison between samples, measurements of contact angle should always be made at similar times after application and at similar air temperatures and humidities. In the method used by Henriques (1992) a photograph of a water drop of volume 0.004 mL is taken. The height and the length of the droplet are measured and the contact angle calculated using:

$$\emptyset = 2 \text{ arctg } 2h/a$$

where,

h = the height of the droplet
a = length of the droplet
$\emptyset$ = contact angle (in radians).

Honsinger and Sasse (1991) suggest that a surface should be defined as hydrophobic for contact angles over 90°. It has been noted that contact angles may vary in the days after application of the product (Henriques, 1992).

(e) Water absorption

Water absorption may be measured by a number of methods including:

total immersion of samples, by measuring the uptake of water into samples by capillarity, by measuring the time taken for a droplet to be absorbed or by measuring uptake through a pipe. Henriques (1992) noted that different methods for measuring water absorption may yield very different results. He suggested that the alkalinity of samples could influence the results obtained.

(i) Immersion water absorption

Standard test methods for water absorption can be found in ASTM C 97 (1977).

Water absorption may be measured by immersing the sample in water for 48 hours (immersion water absorption) and measuring the weight change (Ciabach and Lukaszewicz, 1993; Villegas and Vale, 1992).

$$N_w = [(m_1 - m_0)/m_0]\ 100\%$$

where,

N_w = water absorption

m_0 = mass of sample before impregnation

m_1 = mass of sample after impregnation

(Ciabach and Lukaszewicz, 1993).

Where a material surface is in contact with free water, the absorption follows the equation:

$$m = At^{1/2}$$

where,

m = amount of water absorbed (kg/m^2)

t = time (s)

A = coefficient of water absorption ($kg/m^2.s^{1/2}$)

(Moropoulou *et al.*, 1992).

(ii) Capillary water absorption

Measurements of water uptake or capillary water absorption quantify uptake as water absorption resulting from capillary or adsorptive forces due to wetting of a surface without any external pressure. Data on water uptake are related to those on contact angle since capillary forces increase with reduction in contact angle.

A method for measuring capillary water absorption may be found in BS 6477. A methodology is also given in the NORMAL document 11/85.

The surface to be tested is immersed in water allowing suction vertically upwards. Change in weight over time is measured until the weight remains constant. Weight change may also be monitored throughout drying (Littmann *et al.*, 1993; Sasse *et al.*, 1993). Capillary rise may also be measured by standing the sample in a liquid and observing how rapidly the liquid rises through the stone (Ciabach and Lukaszewicz, 1993; Villegas and Vale, 1992) or by laying samples onto a water saturated sponge for 24 hours (Caselli and Kagi (1995). Gauri *et al.* (1976) used a method in which the sample has two smooth surfaces prepared using 400 grit carborundum, normal to the atmosphere exposed face. The sample is cleaned ultrasonically. One of the smooth surfaces is brought into contact with a soaking wet cloth in a dish. Capillary rise of water is recorded over time.

In the method of Henriques (1992) water absorption compares absorption through treated and untreated faces. The water absorption (%) is measured as the ratio (by mass) between the amount of water absorbed by capillarity through the test faces over 7 days and the total amount absorbed after another 3 days with the non-treated faces immersed in water.

(iii) Water drop absorption time

Water drop absorption time is the time taken to absorb (or evaporate) a drop of water of a given size.

A methodology for water drop absorption can be found in Test No. II.8a, UNESCO-RILEM International Symposium on Deterioration and Protection of Stone Monuments. Paris, 1978.

In the method of Henriques (1992) some changes were made to the above methodology. Water drops of 0.004 mL (rather than 1 mL) were used. Initially an untreated glass surface was used as a reference. However, probably due to differences in surface area of droplets, the water on the glass slide sometimes evaporated more rapidly than the water on the treated samples. A treated glass slide was therefore used as a reference. An expression for water drop absorption was calculated relating the treated to the non-treated surface.

$$\frac{\left[\sum_{i=1}^{m} t_{xi}\right]\left(t_e^{l}.m^{l}\right)}{\left[\sum_{i=1}^{m^{l}} t_{ni}\right]\left(t_e^{l}.m\right)}$$

where,

t_x = absorption time of treated surface

t_n = absorption time of untreated surface

t_e = evaporation time for treated glass surface during tests

t_e^{l} = evaporation time for untreated glass surface during tests

m & m^{l} = number of treated & untreated samples.

(iv) Water absorption through a pipe

In this method (Henriques, 1992) tests are conducted on horizontal surfaces to which pipes had been applied. This test method is said to simulate the situation in which wind driven rain is absorbed into a wall under low pressure. The amount of water absorbed in one hour through treated and untreated surfaces is measured and results expressed as a ratio between these two quantities.

(f) Protective efficacy

The protective efficacy is a method for calculating a value for water absorption changes before and after treatment to allow comparison between different treatments.

$PE = ((A_1 - A_2)/A_1) \times 100$

where,

PE = protective efficacy (%)

A_1 = water absorption before treatment (g)

A_2 = water absorption after treatment (g)

(Frediani *et al.*, 1981)

(g) Water depth penetration

The water front may be detected electrically by drilling holes into the stone opposite to the applied water and fitting a Gann HT-95 digital hydromette (Angel Bello *et al.*, 1992).

(h) Hygric dilation

Hygric dilation is a measure of the amount by which a sample swells when it is saturated with water. It is suggested that this should be measured both parallel to and perpendicular to the foliation (Wendler *et al.*, 1992).

(i) Water vapour adsorption

Water vapour adsorption measures the amount of water in vapour form adsorbed by samples at specific temperatures and humidities (Honsinger and Sasse, 1991). The amount of water adsorbed is affected by a number of factors including surface area and pore size distribution. Water adsorption will be reduced if the number of pores smaller than 0.1μm is reduced since it is at this size that capillary condensation takes place (Sasse *et al.*, 1993).

Water vapour absorption involves a number of related properties including diffusion, transmission and permeability. Generally, water vapour adsorption should be reduced after treatment with a consolidant or water repellent due both to hydrophobic effects and to sealing of small pores where capillary condensation could occur. The rate of water vapour absorption might be expected to be related to measurements of drying rates. However, Henriques (1992) has noted that test results can be widely different.

A method for measuring water vapour permeability is given in BS 6477.

Permeability to water vapour may also be measured by the "bicchierino" method (NORMAL 21/85).

The water vapour transmission rate through a sample may be measured using the German standard "wet cup method" (DIN 52615, 1987) (Honsinger and Sasse, 1991; Littmann *et al.*, 1993; Sasse *et al.*, 1993).

In the method of Henriques (1992) thin circular samples are used. The samples are placed on cups. The relative humidity inside the cups is 0% and outside it is 65% (dry cups method). The test is performed first with the samples untreated, then with the samples treated.

Water vapour transmission can also be measured using ASTM E-96. In this method treated and untreated samples are placed in cells partially filled with distilled water. All surfaces except the treated (or control) surface are then sealed. Weight loss (in g/m^2) is measured for 10 days at 23°C, 50% RH (Boyer, 1987).

For thicker materials such as stone slabs, ASTM C-355-64 (73) is used. Slabs of rock (Biscontin and Riva (1981) used pieces of 110 x 210 x 10 mm) are fixed, using paraffin wax, to the edge of a cup approximately 200 mm in width and 30 mm in depth (dimensions dependent on sample size and permeability). the cup is filled with water and contains blotting paper or cotton wool to prevent water movement wetting the rock. The whole system is placed into a $CaCl_2$ anhydrous desiccator and kept at a temperature of 20 ± 1 °C. Weight change is measured every 24 hours. Good temperature control is critical as small differences in temperature can cause large variations in rate of water loss.

Water vapour permeability may be estimated using:

$$g = \partial / d\,(c_1 - c_2) = \frac{c_1 - c_2}{Z}$$

where,

c_1, c_2 = water vapour concentration at the surfaces
∂ = water vapour permeability
Z = diffusion resistance

(Moropoulou *et al.*, 1992).

(j) Water evaporation rate

In the method of Henriques (1992) non-treated faces of specimens are immersed in water to a depth of 10 ±1 mm for 72 hours. All faces other than the treated face are then sealed with an impermeable material and mass losses are measured over 7 days.

The method of De Witte *et al.* (1985) involved soaking samples for 2 hours in water then wrapping them in aluminium foil leaving only the consolidated surface uncovered. The sample is stored at 20°C, 55% RH and evaporation rate of moisture is measured by weighing at intervals.

(k) SEM characterisation

A number of researchers have examined polymerised stone samples using electron microscopy to characterise the morphology of the bonding between grains. Charola *et al.* (1984b) examined consolidated limestones. With limestones, it is possible to etch the surface using HCl and expose to structure of the consolidant.

(l) Climatic chamber simulations

Climatic chamber simulations can measure vulnerability to thermohygric variations, sunlight, gaseous pollutants or salts (Chiavarini *et al.*, 1993; Rossi-Manaresi, 1981).

(m) Vulnerability to acids or alkalis

The samples may be placed in an acidic or alkaline solution for a set period of time to measure their vulnerability to acids or alkalis. For example, Piacenti *et al.* (1992) placed samples in acid or alkaline solutions for 72 hours. The break down of an applied polymer was measured by FT-IR spectrometry.

(n) Salt crystallisation test

The salt crystallisation test measures the vulnerability of a stone to decay due to crystal growth and expansion within the pores. It is intended to simulate the long term weathering of stone when exposed to natural conditions.

The sample is repeatedly immersed in sodium sulphate solution and oven dried over a number of cycles. Weight loss, or the number of cycles that result in disintegration, is measured. The detailed methodology can be found in Ross and Butlin (1989) or in ASTM C-88 or DIN 52111 (Villegas and Vale, 1992).

(o) Freeze-thaw test

The vulnerability of a stone to freeze-thaw damage may be assessed using the method of procedure A of ASTM Method C 666. Specimens are cycled between -18°C and 22°C with a cycle time of 4 hours for 1000 cycles (Clifton, 1984).

Using the method of Nishiura *et al.* (1984) the stone is saturated with water under vacuum for 24 hours then cycled from -10°C to +10°C on one day cycles for 10 days. Nishiura *et al.* (1984) suggest that ultrasonic propagation velocity may be used to estimate a stone's vulnerability to frost. Nishiura *et al.* (1984) suggest that vulnerable stones have a porosity >20% and an ultrasonic propagation velocity of < 2 kms^{-1}.

Changes in resonance frequencies are measured using ASTM C-215.

Alternatively, according to the methodology of De Witte and Bos (1992) stone samples are placed in a box which has been lined with 4 cm of polystyrene and filled with wet sand. Evaporation of water and frost attack are only allowed to occur through one exposed face. In a climatic chamber the samples are exposed to cycling for 15 hours at -10°C and 9 hours at 15°C, 95% RH. Samples may also be tested after soaking in salt solution.

(p) UV test

Polymers should be tested for vulnerability to breakdown in UV light (<290 nm).

- Piacenti *et al.* (1985) used a Phillips TUV45W lamp for 48 hours.
- Piacenti *et al.* (1992) used 125 watt lamps emitting in the 200-365 nm region at 25 cm distance from the samples.
- Biscontin and Riva (1981) used a mercury lamp at 500 W for 24 hours.
- Cavaletti *et al.* (1985) used UV radiation at 366 nm for 500 hours.
- Gauri *et al.* (1976) used a pen-ray lamp having 90% of its output at 254nm.

A number of methods may be used to detect effects of UV including FT-IR spectra (Chiavarini *et al.*, 1993), measurement of colour changes (Chiavarini *et al.*, 1993), UV spectrophotometry (Gauri *et al.*, 1976) and contact angle measurements (Gauri *et al.*, 1976).

(q) Degradation rates

FTIR may be used for monitoring the rate of deterioration of polymers (Chiavarini *et al.*, 1993).

(r) Colour changes

Colour changes may be assessed by visual comparison with untreated samples or quantified with a chroma meter. A standard test method for visual assessment of colour differences can be found in ASTM D-1729 and a method for instrumental evaluation in ASTM D-2244.

(s) Thermal expansion

Since differences in the thermal expansion and contraction of materials could lead to failure it may be considered necessary to measure this property. A methodology can be found in ASTM E-289.

(t) Efficacy of consolidation

A number of investigators (Clifton, 1984, De Witte and Bos, 1992) test consolidants by using them to consolidate crushed stone, reasoning that this is the ultimate test of a consolidants ability to fix decayed stone.

(u) Surface hardness

A non-destructive test for surface hardness is the Brinell hardness test.

Hardness may be measured by the Clemens Hardness Tester (De Witte *et al.*, 1985). This uses a knife with a load of 300 g to scratch the surface. The change in scratch width between treated and untreated surfaces is calculated as a percentage improvement.

Hardness may also be measured using microsandblasting (Phillips, 1982). In this method standard distances and pressures are used to sand blast surfaces for a set time. The depth of erosion is then measured. In the method as described by Price (1984) an air abrasive gun is used at a distance of 100 mm from the stone surface. A thin sheet of metal with a 7 mm diameter hole in it is placed over the stone. The abrasive was silica sand of 100 FG mesh. The abrasive gun nozzle was 5 mm in diameter and the pressure used was 40 psi (276 kPa) for 2 minutes. Several positions may be measured. The size of the holes produced may be measured by filling them with some suitable powder (e.g. 120-mesh carborundum grit) and weighing the amount.

Hardness has also been assessed by measuring the depth of penetration of a standard drill bit after a set number of revolutions (De Witte and Bos, 1992). This method does not work well on inhomogeneous samples.

(v) Strength tests

The strength of consolidated stone may be measured by a variety of methods.

(i) Bending strength

Successful consolidation should impart a higher bending strength to the stone. Natural stones are generally very inhomogeneous with respect to this test. Bending strength is measured by flexural tension tests (Littmann *et al.*, 1993).

(ii) Splitting tensile strength

Measured by a split test (Nishiura *et al.*, 1984) according to the equation:

$$T = \frac{2P}{\pi d l}$$

where,

T = splitting tensile strength (kg/cm^2)

P = maximum load (kg)

d = diameter of test piece (cm)

l = length of test piece (cm)

A methodology can also be found in ASTM C-190.

(iii) Modulus of elasticity

This characteristic is manifested as the "brittleness" of a material. It is controlled by degree of filling of pores and by the mechanical characteristics of the polymer system (Littmann *et al.*, 1993).

(iv) Modulus of rupture

This test, used by Wheeler *et al.* (1992) after the method of Pardenek *et al.* (1988), involves a three-point bend configuration. Details are available in ASTM C 674-81.

(v) Pull off strength

No details given of method (Auras, 1993).

(vi) Compressive strength

Compressive strength is measured in a hydraulic press (Ciabach and Lukaszewicz, 1993). A standard test method for compressive strength can be found in ASTM C-170 and C-365(1976). The test may be performed on both water saturated and dry specimens as the compressive strength may differ.

(w) Radioactive labelling for determination of decay rates

Šrámek (1989 and 1993) describes a technique he has used to determine the rate of attack on minerals in stone treated with consolidants and water repellents by pollutant gases. Small samples of stone under vacuum are subjected to a high frequency plasma beam of ^{85}Kr ions (energy approx. 100 kV). The ^{85}Kr ions become trapped in crystal lattices of minerals in the stone and are released only very slowly unless the mineral is subject to decay. When the samples are subjected to pollutants, the degree of attack on minerals can be measured by measuring the fall in radioactivity in the stone (see Section 2.2.1).

(x) Vulnerability to biological decay

Vulnerability to biological decay may be measured using the ASTM methods ASTM D684-54 and ASTM G21-70 using agar plates and soil burial tests (Nugari and Priori, 1985).

(i) Tests on inert support media

Using the agar plate test (ASTM G21-70, Nugari and Priori, 1985), test pieces of acrylic cloth were impregnated with the consolidant. They were left in a climatic chamber at 23°C, 55% RH for 48 hours. For each test, five treated and five control samples were weighed and inoculated with fungal strains. The mineral support media used were Nutrient Salts Agar at pH 6.2 and Nutrient Salts Agar + 3 g/l cellulose powder at pH 6.4. At the end of the incubation period a visual estimate of the growth was made, samples were disinfected with a 50% solution of ethanol in water for 20 minutes, washed free of growth and debris by gently rubbing between the fingers in a stream of tap water, rinsed, air dried overnight, then conditioned in a climatic cabinet for 48 hours at 23°C, 55% RH. Samples were then re-weighed and weight losses calculated.

Using the soil burial test (ASTM D684-58, Nugari and Priori, 1985), test pieces of acrylic cloth were impregnated with the consolidant. They were left in a climatic chamber at 23°C, 55% RH for 48 hours. For each test, five treated and five control samples were weighed and inoculated with fungal strains. Samples were buried in a microbiologically active soil at pH 6.0. Control of the microbiological activity of the soil was made on filter paper strips with the same dimensions as the treated cloth. A blank test was made with the same soil, sterilized in an autoclave for 2 hours at 121°C. Incubation was carried out at 28°C, 90% RH for 4 weeks. At the end of the incubation period a visual estimate of the growth was made, samples were disinfected with a 50% solution of ethanol in water for 20 minutes, washed free of growth and debris by gently rubbing between the fingers in a stream of tap water, rinsed, air dried overnight, then conditioned in a climatic cabinet for 48 hours at 23°C, 55% RH. Samples were then re-weighed and weight losses calculated.

(ii) Tests on polymer films

With suitable polymers, test samples can be hardened into thin polymer films and cut to size (40 x 20 mm, Nugari and Priori, 1985) for testing. Thickness may be variable. Test pieces were left in a climatic chamber at 23°C, 55% RH for 48 hours. Weighed specimens (5 treated and 1 control) were inoculated with a mixed fungal inoculum and placed on Nutrient Salts Agar containing 15 g/l glucose at pH 6.4. Samples were incubated for 21 days at 28°C, 90% RH. At the end of the incubation period a visual estimate of the growth was made, samples were disinfected with a 50% solution of ethanol in water for 20 minutes, washed free of growth and debris by gently rubbing between the fingers in a stream of tap water, rinsed, air dried overnight, then conditioned in a climatic cabinet for 48 hours at 23°C, 55% RH. Samples were then re-weighed and weight losses calculated.

2.4 Conclusions

It is difficult to draw general conclusions from the available data on consolidants and water repellents since, although much work has been done, many different stone types, application methods and tests have been used. Much of the literature available is merely descriptive of particular applications of consolidants under uncontrolled conditions. The longer term effectiveness of such treatments is not open to assessment in a scientific manner.

In the literature, opinion is divided on whether the use of water repellents can reduce the rate of decay of stone.

It is however clear that any material which completely blocks surface porosity will lead to accelerated stone decay and such materials should not be used.

While water repellents can prevent or reduce ingress of liquid water through the stone surface they cannot prevent ingress of water in the vapour phase, through cracks at mortar joints, by rising damp or by transfer from surrounding stonework. It may therefore be expected that, although a water repellent could reduce the amount of moisture in a stone, it cannot guarantee to exclude all moisture and, given that many applied materials reduce the rate of evaporation of moisture from a stone, it is not clear that a water repellent will reduce the duration of dampness in a stone.

Where soluble salts are present in a stone these will be dissolved in any liquid water and redeposited when the liquid evaporates. In the untreated stone, capillary forces generated by evaporation of water at the surface will cause these salts to be deposited on the surface where they may do little harm, although salts may also be deposited below the surface, leading to spalling. In a water repellent treated stone, water cannot move out to the surface and must evaporate inside the stone, most probably at the limit of penetration of the water repellent. This will result in the deposition and concentration of soluble salts in this zone. Damage to the stone through crystal growth pressure or volume changes on hydration/dehydration may then occur. A number of treatments including silanes, acrylics and polyurethanes have been found to increase the vulnerability of sandstone to decay linked to salt crystallisation (Caro Calatayud *et al.*, 1992; De Witte and Bos, 1992; Pavia Santamaria *et al.*, 1992; Valdeón *et al.*, 1992; Villegas and Vale, 1992) although, in a number of cases, a decrease in vulnerability was noted (Villegas and Vale, 1992).

Although it is difficult to draw too many conclusions due to the different testing regimes used by different investigators, a common factor on a number of occasions in which the sandstone had increased vulnerability to salt crystallisation appears to be low penetration of the polymer (never more than 7 mm where data is available). Changes to water absorption and drying rates show no obvious pattern with respect to salt decay processes. In two cases (where appropriate tests were performed) silanes were found to increase the vulnerability of sandstone to decay processes caused by acid mists (De Witte and Bos, 1992). In the light of the available evidence, it would seem advisable that where significant amounts soluble salts are present (or may come to be present in a stone) water repellent treatments should not be used.

Problems with salt deposition in a stone may be the result of changes in the porosity of the stone. Changes in porosity which lead to an increase in the proportion of microporosity can increase vulnerability to both salt and frost damage. This has been found with at least one silane treatment although tests for frost vulnerability are not carried out so often as testing for damage due to salts deposition. Changes to porosity are bound to occur where material is being deposited in the stone and the effects of this are not easily predictable. However, the most successful treatments are likely to be those which least alter the characteristics of the treated stone leaving it similar in its behaviour to underlying sound stone. Very few of the polymer materials tested caused large changes in total porosity although changes in water repellency and pore size distribution can significantly alter water absorption and evaporation rates.

Many so-called consolidants also have some water repellent characteristics (e.g. alkylalkoxysilanes) and even some which are not intended as water repellents can substantially reduced rates of water absorption and evaporation. The same concerns should be extended to these as to purely water repellent treatments. For consolidants which have no water repellent component some concerns may also be raised. As with water repellents, the consolidant should not completely block the surface porosity as this will lead to spalling of the surface.

Some consolidants and water repellents-consolidants have been found to be capable of achieving substantial increases in strength in treated stones (Ciabach and Lukaszewicz, 1993; Littmann *et al.*, 1993; Price, 1981; Rossi-Manaresi, 1981; Saleh *et al.*, 1992; Snethlage *et al.*, 1989; Wheeler *et al.*, 1992; Zinsmeister *et al.*, 1988). It is not necessarily the case that stronger is better since, in general, the only requirement of the consolidant is to reduce the rate of decay of the stone surface by re-cementing loosened grains. The surface is not generally required to bear any loads and does not therefore require to be particularly strong. Over-strengthening the surface could lead to other problems, for instance, differences in thermal expansion, blockage of porosity or increased brittleness. Hosek and Panek (1985) suggest that differential thermal expansion could be much more important than is commonly thought as a possible mechanism leading to spalling of treated layers since the degree of thermal expansion of many polymers is much larger than that of rock forming minerals.

The depth of penetration of any consolidant or water repellent is an important factor. As has been stated above

(Section 2.2) it has been suggested that treatments should penetrate at least 25 mm (Price 1975, 1981; Richardson, 1995) or to the depth of stone deterioration (Boyer, 1987; Lewin and Wheeler, 1985; Torraca, 1976; Zinsmeister *et al.*, 1988) to avoid forming a surface layer with different characteristics to the body of the stone and it appears (see above) that where penetration depth is low, problems can arise with salt crystallisation or frost damage below the treated layer. In the available literature, values for penetration can vary widely between polymer materials and for the same polymer in different situations. This makes it difficult to draw any general guidelines regarding depth of penetration but, using the suggestion of Price (1975, 1981) that penetration should be at least 25 mm, only a few silane and polyurethane treatments would be considered effective. Acrylics, epoxies and perfluoropolyethers all exhibited poor penetration where this data was available.

Depth of penetration depends on a number of factors including the stone porosity and permeability, the method of application and the characteristics of the applied consolidant or water repellent. Viscous polymer solutions may have poor penetration but in solutions of low viscosity the polymer solution may migrate to the surface before polymerisation is complete. Generally, the treatment should remain mobile in the stone for a few hours after application to allow time for adequate penetration (Littmann *et al.*, 1993). Problems with solution migration may be avoided by gelation of the solution in the stone prior to polymerisation (Kwiatkowski, 1985) although this must not occur too rapidly or there will not be sufficient time for the solution to penetrate the pore system of the stone (Lewin and Wheeler, 1985). Kwiatkowski (1985) states that polymer gelation may be achieved by using mixtures of alcohol with solvents, causing dissolution of the polymer formed in the reaction medium.

It has been suggested that protective treatments should retain their plastic behaviour throughout the range of temperatures encountered on the stone surface. That is, the glass transition temperature of the material should be above about -20°C (Sasse and Honsinger, 1989) or -30°C (Sasse *et al.*, 1993). It is not clear why this should be required as the stone itself does not exhibit plastic behaviour.

Many treatments were noted to cause colour changes to sandstone. It is likely that any visually noticeable colour change would be unacceptable on a facade, especially if only part of the facade were to be treated. Treatments leading to darkening of the stone included silanes, acrylics, epoxies and polyurethanes (Caro Calatayud *et al.*, 1992; Clifton, 1984; Lukaszewicz *et al.*, 1995; Pavia Santamaria *et al.*, 1992; Price, 1981; Rossi-Manaresi, 1976b; Saleh *et al.*, 1992; Rossi-Manaresi *et al.*, 1995; Wheeler *et al.*, 1992) although not all treatments resulted in colour changes. White deposits were found with some silane treatments (Lukaszewicz *et al.*, 1995; Rossi-Manaresi, 1981; Rossi-Manaresi *et al.*, 1995; Saleh *et al.*, 1992; Wheeler *et al.*, 1992) and with one mixed epoxy-silane treatment (Rossi-Manaresi, 1981). Glossiness may occur due to deposition of polymers on the stone surface and has been observed with at least one silane treatment (Clifton, 1980; Price, 1981).

Colour changes may also occur due to changes in the characteristics of the polymer over time. Polymer materials vary in their vulnerability to degradation but some, including some acrylics, epoxies and polyesters, degrade rapidly when exposed to ultra-violet radiation. Degradation may cause yellowing of the polymer (Clifton, 1980; Horie, 1987; Koblischek, 1985; Šrámek and Králová, 1981) and can lead to failure of the consolidation. Silanes are generally very stable.

Sasse *et al.* (1993) and Saleh *et al.* (1992) examined consolidant treated sandstones by scanning electron microscopy. Honsinger and Sasse (1991) and Sasse *et al.* (1993) found that polymer films of silanes, polyurethanes, epoxy resins, acrylic resins, fluorocarbons and polyesters ranged from a few nannometres to a few microns in thickness. The film formed bridges bonding grains together and while they could fill micropores (<5 μm) (e.g. sealing the micropores between crystals of clay minerals) they did not generally seal capillary pores (<0.1 μm) and larger pores were virtually unaffected. In contrast, Saleh *et al.* (1992) found that the distribution of polymers depended on their composition. In acrylic treated sandstone the polymer film took the form of a fine membrane coating of spongy appearance. In two silane treated sandstones the polymer had either precipitated in nodules or formed a good network around grains and through pores. Where a mixture of acrylic and silane was used the consolidant produced a good coating at grain boundaries and through pores. A siloxane treated sandstone produced only a thin polymer coating and fine cracks were left unfilled. Where an acrylic-silane was used nodules of polymer formed on grain surfaces and particles of polymer were precipitated in pores.

The effective life span of treatments is very little studied. Only two papers have examined the effectiveness of treatments beyond one or two years (Rossi-Manaresi *et al.*, 1995; Snethlage *et al.*, 1989). It is not possible to draw any general conclusions from the little data available.

Some characteristics of particular polymers make them unlikely to be suitable for long term use on buildings. These include polymers which cause distinct colour changes to stone or which are unstable under ambient conditions (e.g. light, temperature, moisture). Opinion is divided with respect to the use of water repellent materials since they alter the characteristics of the stone with respect to water absorption and evaporation. With respect to both water repellents and consolidants there is no agreement as to what represents an appropriate treatment depth. Some investigators suggest that water repellents might be most appropriately applied only to the immediate surface, whereas others suggest that deep treatments are most appropriate. For consolidation, there is agreement that treatments confined to the outer surface are dangerous since they can result in spalling of the stone but there is no agreement on what would be an appropriate depth of treatment beyond the fact that it is obviously necessary to treat the stone deeply enough to consolidate the full thickness of the decayed zone. Some stone consolidants also have water repellent properties. Since it is dangerous to confine consolidation to the near surface this makes the use of a combined water repellent-consolidant problematic if it is considered best to confine water repellency characteristics to the outer surface.

The ideal polymer for use in stone consolidation would be one which can reverse the degradation of a stone, returning it as nearly as possible to its original condition. In order to achieve this the treated stone should mimic sound stone in as many characteristics as possible. Some characteristics are, however, more important than others. The most important include porosity, permeability, colour, thermal dilation and resistance to abrasion. Of all the polymers tested, silanes seem to hold out the most promise although they may not be suitable in every situation. The theoretical end product of polymerisation of the simplest silanes is silica which is present as a cementing mineral in many sandstones and may mimic the behaviour of a natural cement more closely than many other polymers.

In accelerated weathering tests, disintegration occurs in many cases through penetration of fluids and salts behind the treated surface. If in laboratory simulations the sample cubes are too small, so that complete penetration of the treatment occurs, leaving no untreated centre, this would not be a valid test with reference to in situ behaviour where the thickness of building stones means that no treatment is likely to achieve complete penetration.

Data has been extracted from the literature regarding the depth penetration of consolidants and water repellents. Published data on depths of penetration achieved vary from zero up to about 150 mm. Differences in penetration may be attributed to various factors including the properties of the consolidant / water repellent / solvent, the characteristics of the stone and the method and volume of application. Drawing conclusions from the published data is complicated by the lack of necessary information. For instance, some investigators have measured the depth of penetration but do not note the application method for the consolidant. Others may record the application method but only record penetration as "poor" or "satisfactory". In addition, a number of different methods are used for the measurement of depth penetration. Different methods are likely to yield different results since they measure different characteristics. Despite these difficulties it was still possible to gather some information from published sources. The graph in Figure 4 shows quoted values for depth penetration for different methods of consolidant / water repellent application. This data was gathered from a large number of sources: Auras, 1993; Biscontin *et al.*, 1993; Butlin *et al.*, 1989; Caro Calatayud *et al.*, 1992; Caselli and Kagi, 1995; Ciabach and Lukaszewicz, 1993; Clifton, 1984; De Witte *et al.*, 1985; Hosek and Šrámek, 1992; Kotlík and Zelinger, 1978; Littmann *et al.*, 1993; Pavia Santamaria *et al.*, 1992; Rossi-Manaresi, 1976a; Rossi-Manaresi, 1981; Rossi-Manaresi and Tucci, 1984; Snethlage *et al.*, 1989; Valdeón *et al.*, 1992; Wendler *et al.*, 1992; Zador, 1992; Zinsmeister *et al.*, 1988. Some of these methods are suitable for use only in the laboratory where small samples may be used (i.e. vacuum impregnation or total immersion). Others may be used in the field on buildings in situ (i.e. spray or brushing). From this graph it can be seen that many methods failed to achieve an adequate level of penetration (at least 25 mm (Price 1975, 1981; Richardson, 1995)). The most consistently good method of impregnation was by capillary absorption. This method is suitable for use only in the laboratory where small samples can be placed in dishes of the preservative solution. Most of the methods suitable for use in the field failed to achieve adequate penetration. This points up the importance of using laboratory tests which are a good simulation of the situation which will be encountered in the field if the test results are going to be used as a predictor of the expected outcome on buildings.

Comparing the same data with respect to depth penetration and consolidant or water repellent type (Figure 5) it was apparent that greater penetration depths were achievable with silanes, siloxanes and polyurethanes than with acrylics or epoxies.

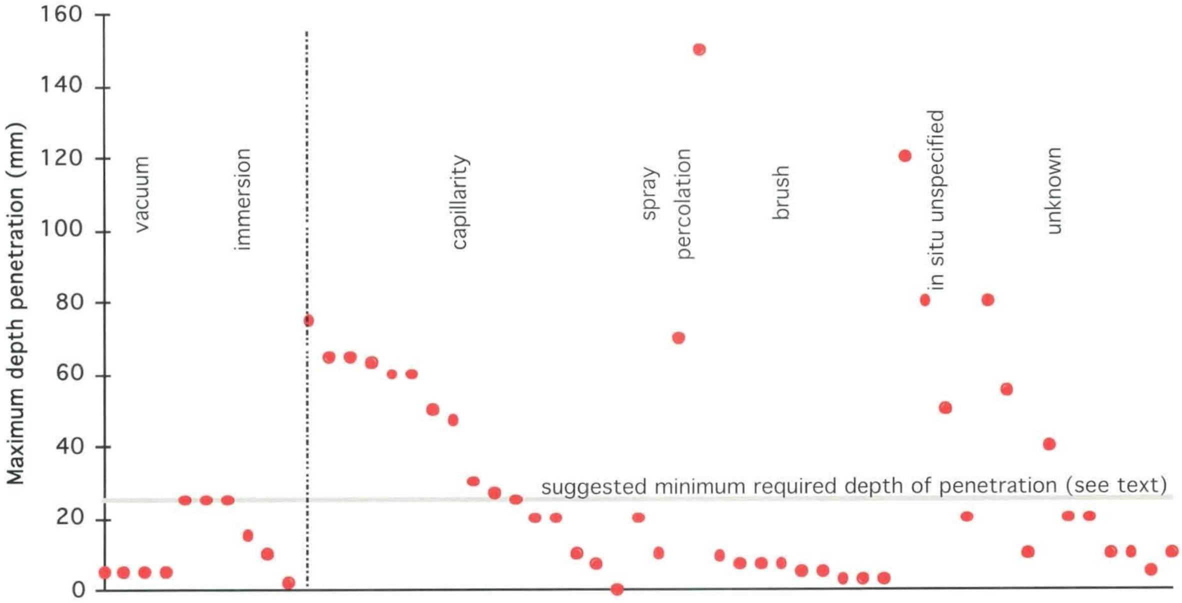


Figure 4 *Depth of penetration of consolidants and water repellents (silanes, siloxanes, acrylics, epoxies and polyurethanes) with respect to application method on various stone types (mainly sandstones and limestones).*

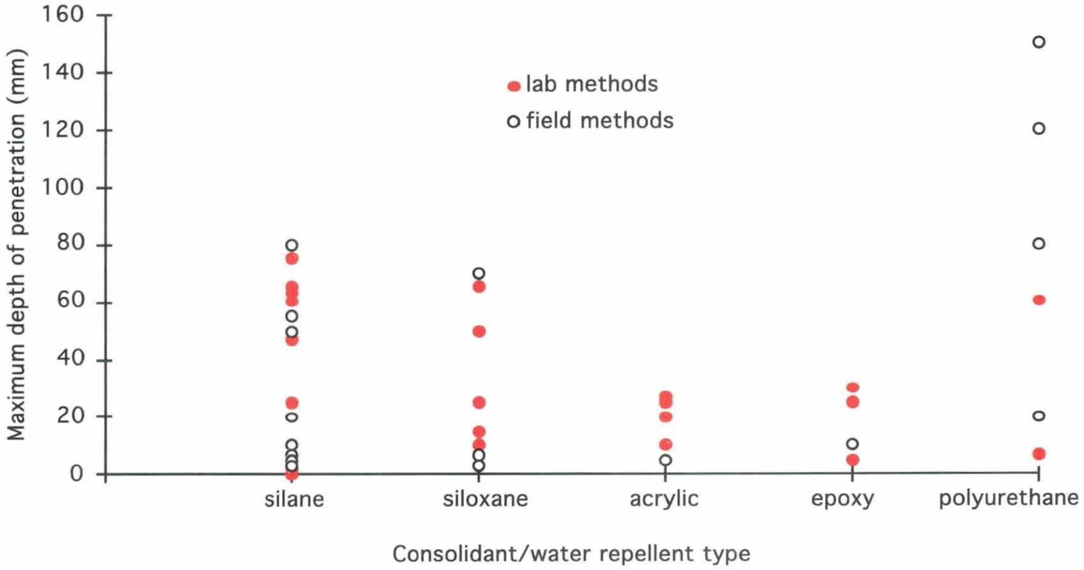


Figure 5 *Depth of penetration of consolidants and water repellents.*

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3 RESEARCH METHODOLOGY

The experimental work was carried out in several parts. Sandstone test panels were constructed at The Robert Gordon University and at Myers Hill (BRE). Cores were taken from the RGU panels for a variety of tests including measurement of colour, water absorption, water droplet absorption, vapour permeability, etc. (Section 3.3). Mature sandstone test panels (approximately seven years old at the time of writing) at The Robert Gordon University were used for examining consolidant-mortar interactions. Some small scale laboratory testing on other sandstone and mortar samples was carried out independently of test panels. The methodologies for testing are given in Section 3.3. Results are given in Section 4.

3.1 Sample organisation and collection

Sandstones were obtained for the research from a number of sources and included both soiled and fresh sandstone. Sandstones were obtained from both Scottish and English sources as some English sandstones are frequently used in the repair of historic buildings in Scotland. It was not always possible to determine the source of soiled sandstone but the characteristics of the sandstones have been determined. Fresh sandstones (Locharbriggs, Clashach and Stainton) were obtained from quarries. Soiled sandstones (Leoch, Clashach, Locharbriggs, Cat Castle and Unknowns A, B & C) were obtained from stone yards which retained sandstone from building demolitions. The soiled Leoch sandstones were sawn to obtain fresh sandstone faces. The sandstone panels were constructed in the summer of 1996 using a 1:3:12 cement:lime:sand mortar mix.

Sandstone	Fresh/ soiled	Description of sandstone
Locharbriggs	Fresh	Red sandstone from quarry in Dumfriesshire
Locharbriggs	Soiled	Sandstone obtained from demolition in Glasgow area
Clashach	Fresh	Pale buff sandstone from quarry in Elgin area
Clashach	Soiled	Sandstone obtained from demolition in Elgin area
Leoch	Fresh	Cut from sandstone obtained from demolition in Dundee area
Leoch	Soiled	Sandstone obtained from demolition in Dundee area
Stainton	Fresh	Pale buff sandstone from quarry in north of England
Unknown B	Soiled	Buff sandstone from Stirling area
Cat Castle	Soiled	Coarse-grained, pale buff sandstone. Soiling from exposure of sandstone blocks, not from building demolition
Unknown A	Soiled	Purple-brown sandstone from Edinburgh area
Unknown C	Soiled	Coarse-grained, white sandstone from Paisley area

Table 1 Sandstones used in the construction of test panels at RGU and Myers Hill.

Tests, results and conclusions in research projects have value if there is confidence in the work and how it has been carried out. In this project the physical property tests can produce quantitative and qualitative results which can powerfully compare one treatment, technique or material to another. As a result, recommendations or conclusions arising from the test work, which may influence Historic Scotland policy or future publications, should be judged in the context of the confidence in the research programme.

For the physical property tests it can be very difficult to go back and re-check or extend experimental work. In addition the transfer of samples from Scottish sites to BRE in Watford requires control so not to confuse samples.

The selection of all samples, treatments and preparation for tests at the BRE site were planned before substantial experimental work had been undertaken.

Real buildings

Site work was carried out to sample and analyse treatments which had been applied to real buildings either previously or during this project. The sites used were Arbroath, Dunkeld, Tantallon, and Holyrood Park. Physical property tests used on the samples or buildings were:

- water absorption of the treated surface
- depth of penetration by water absorption tests
- colour changes

Only a few cores were taken so the identification notes could be written on the core together with associated paperwork.

Test panels

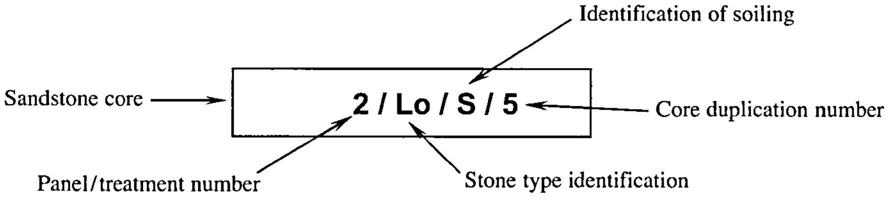
Test panels were constructed to closely simulate real walls and treatment applications. A range of different sandstones were contained within the panels which were representative of Scottish sandstones. Panels were constructed at RGU in Aberdeen and Myers Hill, Glasgow. The exact construction and content of the panels is detailed in Section 4.1 sandstone test panels. The treatments were undertaken as per manufacturers instructions under the supervision of Nick Boyce, a Historic Scotland Conservator. Sampling the sites was carried out by subcontracting stone coring. The stone cores were cut to a size making physical property testing convenient. This was 44 mm diameter, 100 mm length. The physical property tests used on the panels after coring were:

- strength tests
- depth and distribution of treatment by water absorption tests
- water vapour permeability
- UV exposure tests
- freeze-thaw tests
- porosity
- colour changes

Sampling

Samples from the tests panels were used for the BRE physical property tests. The samples required for the physical property tests were taken from the test panels 5 months after treatment. The methodology and amount of sample removal from the test panels was customised for the physical property tests. For each stone type ten cores were required to confidently undertake the physical property tests. 8 stone types were selected together with 2 control stone types. 400 cores were taken in total. The following physical property tests were carried out:

Core numbering and labelling



Panel/treatment number	Stone type identification	Identification of soiling	Core duplication number
1: Panel 1 = untreated control	Lo: Locharbriggs	S: soiled	10 cores were taken from each stone type and labelled 1-10.
2: Panel 2 = Con. A	Le: Leoch	F: fresh	
3: Panel 3 = Water Rep./Con. C	St: Stirling (soiled), or,		
4: Panel 4 = Water Rep. D	St: Stainton (fresh)		
5: Panel 5 = Con. B	Cl: Clashach		

Figure 6 Stone type and identification of surface soiling.

Location of cores in the panels

Photographs of the panels were scanned into computer and enlarged. After some image processing laser printer copies of the panels were made at A4 size. The large, customised size of the prints enabled clear marking of the locations of core holes on site by the coring contractor.

Specification for coring

The following specification was given to the contractors:

Consolidant coring for Historic Scotland; specification for Kirk Natural Stone Ltd.

The experimental stone walls in the quad at RGU in Garthdee Road (Robert Gordon University) are the basis of a research programme that is comparing the performance of a number of stone strengthening products called consolidants. Their use in this context is restricted to valuable carved architectural historical stone that is decaying at an unacceptable rate. The consolidant depth of penetration is between 1-5 cm. Approximately 450 cores are required.

The following ***minimum*** *criteria are required of the cores:*

- *The cores must have a nominal length of 10 cm.*
- *Cores of between 43 and 45 mm diameter are produced using a drill bit 45 mm internal diameter.*
- *Uneven "cracking off" when the cores are removed is allowed as long as 5 cm of complete core is retained on all sides from the surface.*
- *The surface of the core is the most important part, as so must be retained completely intact.*

Specification for the coring contract

- *Power, water and light will be supplied by RGU.*
- *A clear logging and sample recording system will be provided together with plans of the panels.*
- *The contractor will be expected to keep a log book of the work. This will detail arrival and leaving times, number of cores taken per day, the core log numbers, any failed cores and problems encountered.*

The core log number will be recorded using permanent pens (supplied by BRE) five times;

- *on the core*
- *on the hole in the panel*
- *on a paper tag to be applied to the core*
- *in the log book*
- *on plants of each panel and masonry block.*

1. *After each core the contractor will lightly rinse the core in a bucket of water to remove residues, and place the core on absorbent material, clearly marking the core with the reference number.*
2. *The cores will be "collected" by BRE or RGU as they are being cored for the first few days. After this period when the process is clear to all parties, the cores will be collected once or twice a day by RGU or BRE staff.*
3. *The work will be started on the 7th of January 1997 and completed before 31st of January 1997.*
4. *No Saturday or Sunday working.*
5. *Dr Martin Kirk will attend the coring at least once every two days coring to monitor the quality of the work.*

3.2 Application of consolidants and water repellents

Consolidants and water repellents were applied to the test panels as follows:

RGU

Panel 1	Control panel - no chemicals applied.
Panel 2	Consolidant A applied on 26th September 1996.
Panel 3	Water Repellent/Consolidant C applied on 11th October 1996.
Panel 4	Water Repellent D applied on 13th September 1996.
Panel 5	Consolidant B applied on 12th September 1996.

BRE

Myers Hill	Consolidant B and Water Repellent D applied in October 1996
	Consolidant A and Water Rep./Con. C applied in November 1996

3.2.1 Methodologies for consolidant and water repellent applications

The following are the methodologies used for application of consolidants and water repellents to the test panels at RGU and Myers Hill. The methods were taken from manufacturers' instructions but have been adapted to allow measurement of the amount of consolidant or water repellent applied to individual stones. Note that where the treatment was purely a consolidant the treatment was applied to only the sandstone blocks, not to pointing or infilling blocks (although some run-off from the sandstone blocks is likely to have occurred). For water repellent treatments, following measurement of applications to individual stones, the remainder of the front face of the panel was treated with one application. This was to prevent water penetration of the faces of adjacent blocks or pointing which might have influenced the behaviour of the treated blocks in a way which would not be observed in the situation where an entire section of walling was treated in the field.

NB. Some of the chemicals and solvents used are extremely hazardous and should not be handled without appropriate protective equipment. Health and safety information is given in Appendix A2.

Panel 2: Consolidant A

Equipment:

- 5 L Consolidant A
- 5 L methyl ethyl ketone
- 2 buckets

  A plastic bucket as used for applying paint can be used since the solvent (methyl ethyl ketone) in this consolidant should not present a problem. ***Do not use aluminium as it reacts with components of consolidant mix to release hydrogen gas.***
- 2 x 2 inch brush

  Natural bristle brush.
- Aluminium foil sufficient to cover panel
- Polythene sheets sufficient to cover the panel
- Sticky tape for holding down the foil
- Balance

  For weighing the amount of consolidant used in each application. Accuracy to within 1 g is sufficient. Also, you will want some kind of protection between the bucket and balance if you do not want to get gunk on the pan !
- Respirator

  With appropriate filter to deal with methyl ethyl ketone.
- Protective gloves
- Face shield and goggles
- Overalls
- Equipment for recording air temperature and humidity

Methodology for application:

The panel must be thoroughly dry at the time of application. The panel should be protected from direct sunlight for a few hours prior to applications to avoid the surface becoming too warm (will lead to rapid evaporation of solvent). Record air temperature and relative humidity at the time of application. Air temperature should be 10-30ºC. Application of consolidant to individual stones is best done from the bottom up to avoid run-off marking on untreated stones.

Put sufficient consolidant in bucket to treat one stone (about 200 mL or so is usually plenty, maybe more for more porous stones like Locharbriggs).

1. Weigh the bucket + consolidant and record weight (do this just before application as the solvent evaporates fairly fast).
2. Brush on consolidant to saturate the surface, working from top down on an individual stone.
3. Immediately re-weigh the bucket + consolidant and record weight.
4. Repeat steps 1 - 3 twice more at 5 minute intervals (i.e. 3 applications in total).

After 20 – 30 minutes, repeat steps 1 – 4. If necessary, after another 20 – 30 minutes, repeat steps 1 – 4. i.e. 2 or 3 cycles of 3 individual applications making either 6 or 9 applications in total.

If sufficient consolidant has been applied, excess material should remain visible on the surface for 30 minutes following the last application. *Note: This instruction is from the manufacturers' guidance notes. In the laboratory this may be possible, but in the field evaporation rates of the solvent are too fast for any excess to remain visible after 30 minutes. On our test panel we used 2 application cycles on Cat Castle, Leoch, soiled Unknown sandstones A & C since all these had relatively low absorbancy. On all other sandstones we used 3 application cycles.*

Flush excess material from the surface using methyl ethyl ketone. After the final treatment the panel should be covered with foil and polythene overnight to allow time for the solvent to soak in. The foil covering keeps direct sunlight off the stones. After the first night the foil covering can be removed but the polythene sheet should be kept on until the smell of solvent has dispersed (or if any tests are to be done of the stones which require them to be dry). Protect the surface for at least 2 days following application (manufacturers notes). Curing time is at least 2 weeks. Dispose of excess consolidant by pouring into sand or some other absorbent material.

Panel 3: Water Repellent/Consolidant C

Equipment:

- 5 L Water Repellent/Consolidant C
- 5 L white spirit
- 2 buckets

  A plastic bucket as used for applying paint can be used since the solvent (white spirit) in this water repellent should not present a problem.
- 2 x 2 inch brush

  Natural bristle brush.
- Polythene sheets sufficient to cover the panel
- Balance

  For weighing the amount of consolidant used in each application. Accuracy to within 1 g is sufficient. Also, you will want some kind of protection between the bucket and balance if you do not want to get gunk on the pan!
- Respirator

  With appropriate filter to deal with white spirit and silanes.
- Protective gloves
- Face shield
- Air tight goggles

- Overalls
- Boots
- Equipment for recording air temperature and humidity

Methodology for application:

The panel must be thoroughly dry at the time of application. Record air temperature and relative humidity at the time of application. Air temperature ideally should be 10-20°C, RH > 40%. Do not apply in direct sunlight. Application of water repellent to individual stones is best done from the bottom up to avoid run-off marking on untreated stones.

Put sufficient water repellent in bucket to treat one stone (about 200 mL or so is usually plenty, maybe more for more porous stones like Locharbriggs). Weigh the bucket + water repellent and record weight (do this just before application as the solvent evaporates rapidly). Brush on water repellent to saturate the surface, working from top down on an individual stone. Immediately re-weigh the bucket + water repellent and record weight. Apply treatment twice, wet-on-wet. Within one hour of application wash surface with white spirit to avoid discoloration.

After the treatment, the panel should be covered with polythene to allow time for the solvent to soak in. Manufacturers instructions are that treated areas should be covered for up to 3 days after application and that curing time is at least 2 weeks. Dispose of excess water repellent by pouring into sand or some other absorbent material.

Panel 4: Water Repellent D

Equipment:

- 3 L Water Repellent D
- 1 bucket

  A plastic bucket as used for applying paint can be used since the solvent (white spirit) in this water repellent should not present a problem.
- 1 x 2 inch brush

  Natural bristle brush.
- Polythene sheets sufficient to cover the panel
- Balance

For weighing the amount of consolidant used in each application. Accuracy to within 1 g is sufficient. Also, you will want some kind of protection between the bucket and balance if you do not want to get gunk on the pan !

- Respirator

With appropriate filter to deal with white spirit.

- Protective gloves
- Face shield and goggles
- Overalls
- Equipment for recording air temperature and humidity

Methodology for application:

The panel must be thoroughly dry at the time of application. Record air temperature and relative humidity at the time of application. Application of water repellent to individual stones is best done from the bottom up to avoid run-off marking on untreated stones.

Put sufficient water repellent in bucket to treat one stone (about 200 mL or so is usually plenty, maybe more for more porous stones like Locharbriggs). Weigh the bucket + water repellent and record weight (do this just before application as the solvent evaporates). Brush on water repellent to saturate the surface, working from top down on an individual stone. The methodology states that the water repellent should run off 6-10 inches below the stone when sufficient has been applied. Inevitably this results in some overestimation of the amount of water repellent that was applied to the stone but this seems unavoidable. Immediately re-weigh the bucket + water repellent and record weight. There is no repeated application or use of solvent with this treatment. After treatment cover the panel with polythene until the solvent has evaporated. Dispose of excess water repellent by pouring into sand or some other absorbent material.

Panel 5: Consolidant B

Equipment:

- 4 L Consolidant B in toluene (10% w/v)
- 3-4 L toluene
- 2 x small metal buckets or glass jars

  Metal buckets of the kind used for mixing paint will do. Otherwise some kind of glass jar. Do not use plastic buckets as acrylics will react badly to plastic.
- 2 x 2 inch brushes

  Natural bristle due to possible bad reaction with plastic.
- Aluminium foil sufficient to cover panel
- Polythene sheets sufficient to cover the panel
- Sticky tape for holding down the foil
- Small beaker to dip out consolidant from the large tin
- Balance

  For weighing the amount of consolidant used in each application. Accuracy to within 1 g is sufficient. Also, you will want some kind of protection between the bucket and balance if you do not want to get gunk on the pan!
- Respirator

  With appropriate filter to deal with toluene.
- Protective gloves

  Cotton or leather gardening type gloves are probably better than plastic due to possible reaction with acrylic.
- Face shield and goggles
- Overalls
- Equipment for recording air temperature and humidity

Methodology for application:

In practice, tissue is sometimes used to keep fragile fragments in place during application. The tissue is applied to the deteriorated stone using wallpaper paste. This is done well in advance of application of the consolidant so that the stone is dry at the time of application. In these experiments some tissue was used on a few stones but as it could not be applied in advance it was stuck down with the first application of consolidant. In practice, the tissue was difficult to keep on the stone as it tended to lift off during the solvent wash. None of the sandstones used on the test panels was particularly badly decayed and the tissue application appeared to have little effect. However, on severely decayed stone its use might have been necessary to prevent loss of fragile material.

The panel must be thoroughly dry at the time of application. Record air temperature and relative humidity at the time of application. Application of consolidant to individual stones is best done from the bottom up to avoid run-off marking on untreated stones.

1. Put sufficient consolidant in bucket to treat one stone (about 200 mL or so is usually plenty).
2. Weigh the bucket + consolidant and record weight (do this just before application as the solvent evaporates fairly fast).
3. Brush on consolidant to saturate the surface, working from top down on an individual stone. Follow this immediately with a second coat if the first has been quickly absorbed.
4. Immediately re-weigh the bucket + consolidant and record weight.
5. Brush on toluene to saturate the surface, applying twice if first application is quickly taken up. The toluene application is intended to "push in" the consolidant application.
6. Repeat the above procedure (1 - 5) on all the stones in the test panel until they have all received one application.

Repeat the above procedure until all stones have received 3 applications of consolidant and toluene with the exception of Leoch fresh, Leoch soiled and "Unknown A" which receive only 2 applications of consolidant and toluene. When the consolidant application is finished give the whole surface a good saturating brush over with toluene working from top to bottom to avoid leaving run-off marks. After the final treatment the panel should be covered with foil and polythene overnight to allow time for the toluene to soak in. The foil covering keeps direct sunlight off the stones. After the first night the foil covering can be removed but the polythene sheet should be kept on until the smell of toluene has dispersed (or if any tests are to be done of the stones which require them to be dry). Dispose of excess consolidant in the buckets by pouring onto sand or some other absorbent material.

NB. There is likely to be some run-off onto lower stones during consolidant application. Affected stones should be immediately brushed with toluene to disperse the runs and avoid permanent marking.

3.2.2 Characterisation of consolidants and water repellents

Without a detailed chemical analysis, complete characterisation of the water repellents and consolidants is not possible. Manufacturers safety data sheets provide a record of the more toxic components of the treatments (Table 2). In addition to this information, elements in the treatments of atomic weight greater or equal to that of sodium were determined semi-quantitatively using X-ray analysis (Table 3).

Product	Chemical	Solvent/s	Catalyst
Consolidant A	Potassium methyl siliconate (40-50%)	Methyl ethyl ketone (25%)	Potassium hydroxide (3%)
Consolidant A (variety 1)	Tetraethylsilicate (24%)	Butanone (19.5%)	Dibutyltindilaurate (1.5%)
Consolidant A (variety 2)	Tetraethylsilicate (50%)	No data	Dibutyltindilaurate (3%)
Consolidant B	Methylacrylate + ethylmethacrylate (10%)	Toluene (90%)	None
Water Repellent /Consolidant C	Tetraethylsilicate (12.5%)	Butanone (17.5%) Toluene (3.8%)	Dibutyltindilaurate (1.5%)
Water Repellent D	Silicone (5-10%)	Aromatic HC (10-20%) Aliphatic HC (70-90%)	No data
Water Repellent E	Alkylalkoxysilane (50%)	Water	No data
Water Repellent F	Petroleum naphtha (90-95%)	No data	No data
Water Repellent G	Isobutyltrimethoxysilane (95%)	Methanol (2%)	No data

HC: hydrocarbon

Table 2 Compositional data for consolidants and water repellents used in experiments.

Elemental analysis

Table 3 shows the results from elemental analysis of samples of consolidants and water repellents including those used on the test panels. A few drops of each consolidant or water repellent were placed on carbon discs prepared for viewing using scanning electron microscopy (SEM). The discs were kept for at least 5 weeks to allow time for the evaporation of solvents and for polymerisation to take place. The samples were then used for energy dispersive X-ray (EDX) analysis under SEM. This technique can identify the presence of elements of atomic weight greater than or equal to sodium. It cannot therefore detect the presence of carbon, oxygen, hydrogen or other light weight elements in the applied treatments.

	Abundance of element		
Treatment	**Major**	**Minor**	**Trace**
Water Rep./Con. C	Si	Sn, S	Na, Al
Consolidant A (var. 1)	Si	Sn, Cl	
Consolidant B			Si, Al, Mg
Wacker 090			
Wacker 280	Si		Al
Wacker 290	Si	Sn	S, Na
Consolidant A (var. 2)	Si	Sn	Cu, Cl, S, Na
Wacker SMK 1311	Si		Zn, Cu
Funcosil SNL	Si	S	Na, Cu, P, Al, K, (Cl?)
Permarock 5115 LB	K, Si	Al, S	Cu
Wacker BS 1000			
Water Repellent D	Remained tacky - could not be analysed		
Water Repellent F	Remained tacky - could not be analysed		
Water Repellent G	Remained tacky - could not be analysed		

Key

Al - aluminium
Cl - chlorine
Cu - copper
K - potassium
Mg - magnesium
Na - sodium
P - phosphorus
Si - silicon
Sn - tin
S - sulphur
Zn - zinc

Table 3 Results of elemental analysis by EDX of consolidants and water repellents.

3.3 Individual test methodologies and experimental design

3.3.1 Petrological examination of sandstones

Thin sections (30μm thickness) were prepared of samples of each sandstone used in the test panels. These sections were used for petrological examination of the sandstones using a geological microscope. This allows determination of the mineral constituents of the sandstone, including the cement, and their proportions can be estimated. The grain size, shape and sorting of the sandstone can also be determined and information can be gathered on other aspects of the sandstone texture including differential banding, parallel orientation of grains and the nature of porosity (e.g. intergranular or intragranular).

3.3.2 Measurement of colour changes

Colour changes caused by treatments were assessed by measuring the colour of the sandstones before and after treatment. The colour analysis of stone surfaces was done using a chroma meter (Minolta Chroma Meter CR-210). This is a battery or mains powered, hand held device for measuring reflected-light colour. It works best on flat surfaces but may give useful data on rougher surfaces. The analysed area is a circle 50 mm in diameter. The head of the instrument shields this area from incident light and a bright beam of light (pulsed xenon arc lamp) from the instrument is flashed onto the surface. The reflected light is picked up by high sensitivity silicon photocells. The data can be output on various colour scales. The colour scale used here is L*a*b*. The L* data measures the brightness level on a scale of 0% (black) to 100% (white), a* and b* are chromaticity co-ordinates which incorporate both "hue" (colour) and "chroma" (colour intensity or saturation). The a* data runs on a scale of -60 (green) to +60 (red). The b* data runs on a scale of -60 (blue) to +60 (yellow).

3.3.3 Measurement of liquid water absorption rates in the field

The rate of water uptake by relatively porous stones may be measured using a device in the form of a graduated tube with a bulbous bottom, one side of which is open (Figure 7). The open side of the base is sealed against the stone (using a plastic, mouldable adhesive or some other appropriate sealant) and the tube is filled through the open top. Water flows into the stone and its rate of movement is measured by timing the drop in water level inside the tube against the graduations down its side. The surface area through which the water is absorbed is a circle of area 163 mm^2 (the size of the open side at the tube base).

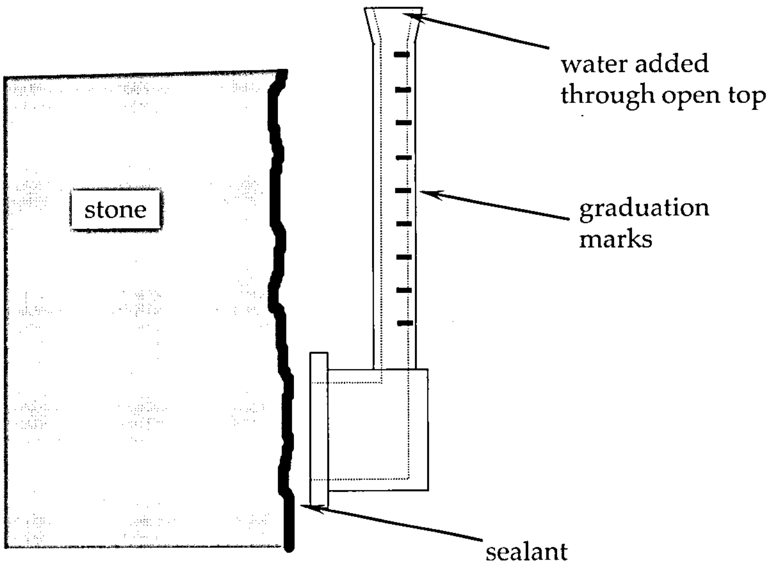


Figure 7 Device for the measurement of water transport rates into stone.

3.3.4 Strength tests

Consolidants are applied to masonry to strengthen the structure of the building surface. To measure strength there is a standard RILEM test for Ultimate Bending Strength (test no iii.6). The test states that it can be used to assess the effectiveness of an impregnation treatment as a method for improving the mechanical strength of stone. Strength (ultimate stress) detects the nature of the critical component (the faulty element) in the intrinsic structure of the rock. The elastic properties of the material are also determined. This type of test is also known as flexural strength.

The RILEM test, as it is published, was considered not suitable for the assessing consolidant treatments in the context of this research project. The samples recommended by RILEM are too large and would not show the surface treatments if they only penetrated a few millimetres; as a result, the RILEM test was customised to resolve the incremental changes in strength at different depths of penetration. To allow a higher resolution the thinnest samples possible were cut. Together with the thickness of the cutting blade, this allowed an incremental resolution of about 5 mm. The test method devised allowed both the ultimate stress and modulus of elasticity to be calculated from the same experiment.

3.3.4.1 RILEM based method for strength test

Treated cores were sliced into discs approximately 3 mm thick with a diamond saw blade. The diameter of the cores was approximately 40 mm. This was carried out incrementally from the surface to beyond the estimated depth of penetration for the treatments. Each slice was then measured by micrometer to determine its thickness (d) in meters. The samples were positioned on two parallel knife edge supports 35 mm apart. The loading point was in the centre of the sample and rounded to form a 5 mm radius. The load was increased slowly. The load applied and the displacement were recorded at several increments. The length of the crack produced (b) was measured with a micrometer in meters. At the point of failure, characterised by fracture or a drop in the recorded load, the last load value and last displacement value were noted.

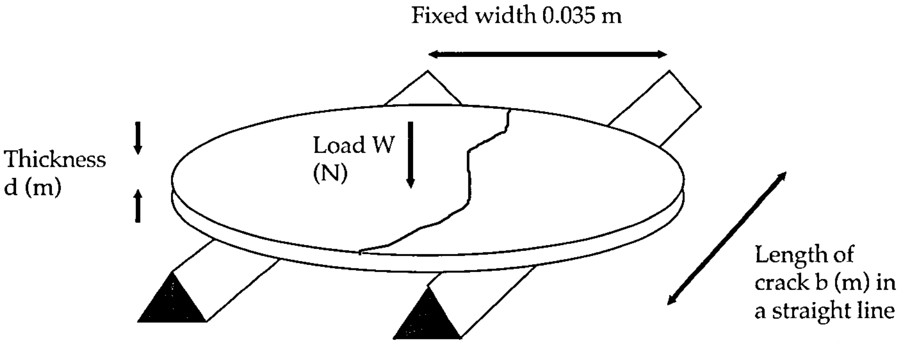


Figure 8 Diagram of fractured consolidant slice on the knife edge testing device.

The modulus of elasticity and ultimate strength were calculated using the following formulae. The formulae take into account the geometry of the samples and theorise a stretching affect on the underside of the slice. The units are comparable with published strength and elasticity data. Several values for modulus of elasticity were calculated on each individual sample to produce an average.

$$\text{Ultimate strength } (\text{Nm}^{-2})\text{x}10^{6} = \frac{0.0525 \text{ x Load at failure (N)}}{\text{b (m) x (d (m))}^{2}} \text{ x } 10^{6}$$

$$\text{Modulus of Elasticity } (\text{Nm}^{-2})\text{x}10^{9} = \frac{0.877 \text{ x Load (N)}}{\text{b (m) x (d (m))}^{3}} \text{ x } 10^{9}$$

The RILEM type of ultimate strength test is likely to produce results similar to a tensile strength test. This is because as slices of sandstone are bent, the top of the slice is in compression, and the underside is in tension. As the tensile strength in stone is usually weaker than the compressive strength, the failure occurs because of the tensile stress.

Compressive strength tests are more complex to devise. The samples must be shaped and designed perfectly otherwise they will also tend to fail through internal tensile stress and give misleading results. In the same way a weathered and uneven sample will act in different ways to compression.

On real consolidated building surfaces it is likely that tensile stress is more important than compressive strength for this reason. If the building surface is put under load it will tend to act like the non-ideal sample, and fail due to tensile stress before compressive. Compressive strength of consolidants would be more important if the treatments were designed to improve the structural properties of the whole buildings. This is not the case in surface applied treatments.

3.3.4.2 Surface hardness tests

In the terms of this report the "surface hardness" is the strength of the various layers which make up the weathered or deteriorated surface together and individually. The surface hardness does not necessarily refer to the very top surface as this is contingent on the layer below it. Friable surfaces of weathered sandstone are often several millimetres in thickness. Surface hardness may therefore constitute a "crust". If the crust is very thin and present on the stone surface the application technique of the treatment will be strongly influential in its existence and strength. The application instructions for consolidants used in this project generally suggest pure solvents are used to "rinse" or "key" in after treatment. The top "slice" in the strength tests was generally 2-3 mm and this was considered suitable for measurement of surface hardness as well as sub-surface hardness.

3.3.5 Depth and distribution of treatment by water absorption tests

To determine depth of penetration of consolidants and waterproofing agents is important. There must be confidence that the treatment, if applied to a weathered or exposed surface, "keys in" to stable masonry underneath. Water absorption tests are an effective method of locating the existence and distribution of some consolidants and water repellents.

3.3.5.1 RILEM based water drop test methodology

In 1978 RILEM produced two standard tests to measure the depth of penetration of consolidants and water repellent agents. These are both based on dropping known volumes of water onto the treated stone and timing the period required for the water to absorb. Generally, the treatments increase the time taken for water to absorb into the stone. The cores taken from the treated panels at Garthdee Road make ideal samples for the RILEM tests.

The two tests mentioned in RILEM are essentially very similar. Tests no ii.8a involves dropping 0.01 mL of water onto the stone and timing the absorption. Test ii.8b involves dropping 1 mL of water onto the stone and timing the absorption. Test ii.8b was unsuitable for this project as 1 mL was far too large a volume. Some of the treatments only penetrated a few millimetres; however, it was also found that 0.01 mL was difficult to work with when undertaking many tests (several thousand individual drop tests were used for this project). The level of variation in practically placing 0.01 mL on a rough stone surface was also too high. As a result the test ii.8a was used but this twice the water volume i.e. 0.02 mL. The RILEM test also does not suggest a statistical approach to testing many cores; as a result, a customised RILEM test was devised for this work programme.

RILEM based water drop test

All cores in the BRE testing programme (400) were clearly labelled and placed in one room to dry for 76 hours. A spread sheet was formulated to log all the cores. Drops of water 0.02 mL were placed using a micro-pipette on the side of the cores at 11 specified intervals. These were: 0-0.1cm, 0.5cm, 1cm, 1.5cm, 2cm, 2.5cm, 3cm, 4cm, 5cm, 6cm and at the base of the core 7+cm. The time taken in seconds for the drop to absorb and any wetness to vanish was recorded (T_{exp}). Time periods of 0-3 seconds were estimated as either 1,2 or 3 seconds without a clock. Time periods of 3-180 seconds were recorded with a clock. Time periods of over 180 seconds were recorded as 180 (evaporation effects begin to dominate after a few minutes).

For each stone type and consolidant type 5 different cores were tested, including the untreated cores. If a high level of variation of results was found 10 cores were tested. Over 200 cores were tested in all. The 11 values produced from each control core were averaged and the standard deviation calculated. The average was added to three times the standard deviation to produce a threshold value ($T_{control}$). If at a particular depth on each core, T_{exp} is higher than $T_{control}$, then it is 99% likely that there is a treatment present at that location (this assumes that the water absorption values from untreated areas of the cores of each stone type have the same average and normal distribution). From comparison of all the data, the maximum depth of treatment on one core is then calculated. In each case 5-10 cores were selected. As a result minimum, maximum and average depths of penetration were calculated.

3.3.5.2 Change in hydrophobicity test methodology

Because of variations and changes in results produced in testing the RILEM based water drop test a more complex RILEM based test was devised. The aim was to assess the variation in hydrophobicity over the core surface, and to detect changes in hydrophobicity in time and the hydrophilic consolidant cured. A large amount of data was required. The test compared the water absorption data from the outside of the core to the freshly cut centre of the core after the core had been stored for 7 months. If there was a difference in the two sets of data this would imply continued slow curing of the treatment or the presence of hydrophobic compounds for some time after application.

Method of test for hydrophobicity change

A treated core of was selected and tested for depth of penetration with the RILEM based water drop test method (Section 3.3.5.1). The core was then stored for seven months covered with a light proof cloth and open to the air. For the second phase of water drop tests, the core was cut in half lengthways. The sample was dried at ambient temperature and humidity for 24 hours. RILEM type water absorption tests were carried out as detailed above on the same surface as before, and also the new freshly cut surface. This comprised 5 strips of tests at 0.5 cm intervals from the treated surface. Each strip was 1 cm apart. Where the test soaked too large an area and encroached on the next increment the sample was re-dried and the missing data taken later. The data was plotted to spatially map the location of each water absorption value. Comparison of the data gives a characterisation to any hydrophobic changes caused in the period of about one year after application.

3.3.5.3 Wetting and drying effects test

The affects encountered in analysis of the water absorption data were further investigated using wetting and drying experiments. A surface will look "wet" because fluids will fill surface pore and scratches. The water reduces the apparent amorphous nature of the surface and creates a wetter, darker look. The extent of wetting will be affected by any consolidants or water repellent agents. This is because the treatments will coat or line the pores of the masonry. This will change the stone roughness and the wetting contact angle. In addition, the rate of subsequent drying may also be affected.

Wetting and drying test methodology

A dry core is quickly "splashed" with just enough water to wet the whole surface. Dry areas may appear immediately or subsequently which denote the location or limit of the treatments. Afterwards a sample is soaked in water for a period of 10 seconds or more. The sample is then left until it appears dry (10-100 minutes). Dry areas may appear which show the location or limit of treatments. Photography or immediate measurement of any effects found is used to record the location of the treatments.

Cores taken from Arbroath, Tantallon and Dunkeld

Cores from the sites which were treated with Brethane based consolidants in the 1970s were tested for hydrophobicity using the water drop tests to find the existence, depth and distribution of consolidants.

3.3.6 Water vapour permeability test methodology

When consolidants are applied to historic surfaces they should still allow any trapped water vapour to pass to the atmosphere. This is so that water cannot build up within the stone and cause dampness problems, accelerated decay and frost damage. There is a British Standard to determine the actual water vapour permeability of materials. BS 31 77:1959. The permeability to water vapour of flexible sheet material used for packaging. The test creates a humidity gradient across the sample. The high humidity on one side of the treated sample passes through the stone into the water absorbing calcium chloride. The weight increase found in the calcium chloride is proportional to the water vapour permeability of the system. Based on this standard the water vapour permeability of the cores was determined from discs of stone approximately 8 mm thick and diameter 44 mm.

Water vapour permeability method

One core from each stone type and treatment type was sliced into discs 7-10 mm thick. Several slices were taken from each core to give roughly 1 cm increments into the treated faces. A small amount (2-3 g) of anhydrous calcium chloride was placed in the bottom of the water vapour test cup. The stone disc samples were sealed with wax into the cups. The cups were then placed in a room at 60% humidity and 20 degrees centigrade.

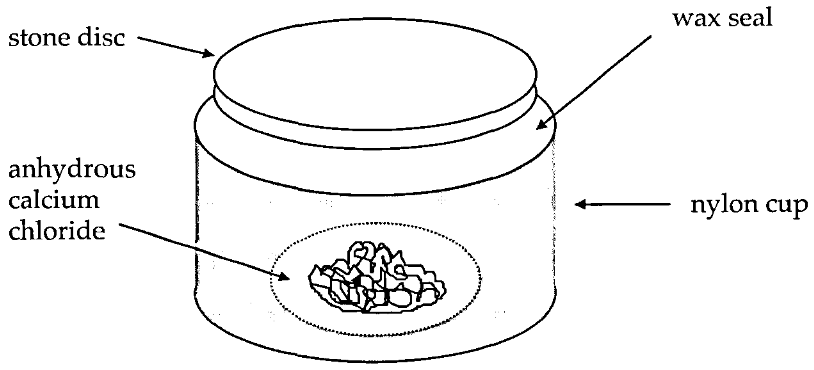


Figure 9 The permeability cup with the stone sample, and a cut away showing the calcium chloride.

The weight increases were recorded twice a day for 7 days. The diameter of the discs and the rate of water absorption against time was measured. This allowed calculation of the water vapour permeability in grams per meter square per day (g m^{-2} day^{-1}). The stone disc sample thickness was found to strongly influence the results with a linear relationship over the range 7-10 mm thickness. The results were normalised using the thickness of the samples to size the permeability for a 10 mm sample thickness.

3.3.7 Exposure tests: ultraviolet light, moisture and freezing

3.3.7.1 Ultraviolet light

Ultraviolet light (UV) can damage some surface treatments, resulting initially in discoloration and finally in cracking and structural failure. As the treatments in this project are generally sub-surface in location structural failure by UV is not considered. Discoloration however could become a serious problem. Two methods of exposure were designed.

Accelerated UV exposure

Accelerated UV testing is only partially representative of real exposure conditions. Increased levels of high energy ultraviolet radiation will cause different reactions in the treatment compared to natural levels of radiation. The results can be considered a pass or fail test of UV sensitivity or a qualitative test guide to what might happen in the future. It can also determine materials that are not sensitive to UV, based on the theory that if the material can withstand the exposure to UV-B, then natural exposure will be much less rigorous.

UV-B test was carried out on a wide range of samples from the test panels. The surface of each core was removed intact with a stone saw and bonded into metal plates in vertical “QUV machines” (machines by Q-Panel Company). and automatically exposed to cycles of UV-B radiation and water condensation cycles.

3.3.7.2 Natural exposure to UV at Myers Hill site

Panels with a wide range of sandstone types were constructed at Myers Hill, near East Kilbride, Glasgow at an altitude of 300m. The location and altitude give a combination of high UV levels and frequent rain and frost events.

3.3.7.3 Freeze-thaw tests

To determine if frost cycles will affect treated sandstone freezing and thawing tests were carried out. Cores of pre-treated Locharbriggs, Clashach and Leoch, Stainton and the Stirling sandstone were selected. The range included both weathered and fresh surfaces. The treatments were Con. A, Water Rep./Con. C, Water Rep. D and Con. B. All cores were subjected to 110 cycles of freezing and thawing in an automated freeze/thaw chamber. Each cycle lasts 140 minutes. A Weiss Technik KWP/450/70 water tank chamber was used.

3.3.8 Dilatometry

To determine if consolidation of porous stone causes expansion or contraction of the masonry dilatometry experiments were undertaken. 5 cores of Locharbriggs sandstone were dried at room temperature and humidity and the length was measured between two positioning studs (Demet points) 5 cm apart. Two measurements were taken from studs on opposite sides of each core as shown in Figure 10 with a dilatometer. The cores were submerged in Con. A, Water Rep./Con. C, Water Rep. D and Con. B for 5 minutes to simulate treatment. One core was left untreated. Afterwards the dilatometry measurements were taken again. Measurements were subsequently taken at different times in the drying and curing process. The effect of soaking the treated cores with water was also analysed.

The dilatometry work may produce different results on different stone types. This work concentrated on Locharbriggs sandstone. There is good justification for this as Locharbriggs has a high porosity, and has shown in past tests to absorb the largest amount of treatment. Locharbriggs was also the weakest in structural tests. It was therefore considered the most likely stone to exhibit dimensional changes.

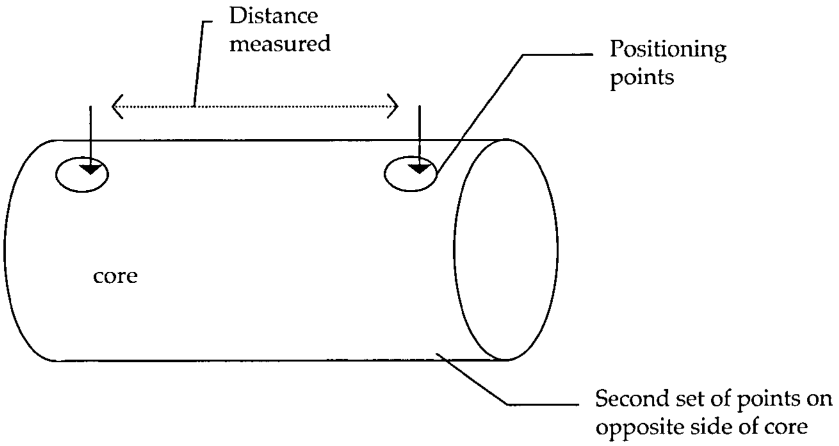


Figure 10 Positioning of the Demet points on sandstone cores for dilatometry.

3.3.9 Emission of volatile organic compounds (VOCs)

The water repellents and consolidants used may emit by evaporation unwanted residues of solvent, active ingredients, reaction products and water when drying and curing. Manufacturers instructions warn of the hazards involved and give suitable health and safety instruction. There is, however, less information about the exact nature and identification of the chemicals emitted. As a result the identification of possibly hazardous emitted compounds was carried out.

Experiments measuring weight loss following treatment (due to evaporation of solvents and treatments) were carried out by both BRE and RGU. Methodologies differed and are reported below in Sections 3.3.9.1 (BRE) and 3.3.9.3 (RGU).

3.3.9.1 Total solvent loss (BRE methodology)

The evaporation of residual consolidant and water repellent solvents, reaction products and active ingredients was most easily monitored by weight loss of samples after treatment. This will however also include loss of water produced by reaction. Samples of Locharbriggs sandstone were treated with Con. A, Con. B, Water Rep./Con. C and Water Rep. D. To simulate real treatment conditions the following experimental procedure was used for the treatment weight tests.

Experimental procedure

Cores were left at room temperature and humidity overnight and weighed. The cores were placed face down in a shallow tray containing a depth of 2-3 mm of each consolidant/water repellent. The samples were left until the treatments had soaked up the core to a height roughly correlating with the experimental depths of penetration found on the panels. The cores were removed and excess treatment wiped away. The cores were weighed to record the weight of treatment absorbed. The cores were then wrapped in foil on all sides except the treated face and weighed again to give the weight of foil. In this test, weight loss was recorded every hour for the first two days, and then at greater intervals as the rate of evaporation reduces. The weight losses can be converted to show the weight of original consolidant remaining, and plotted.

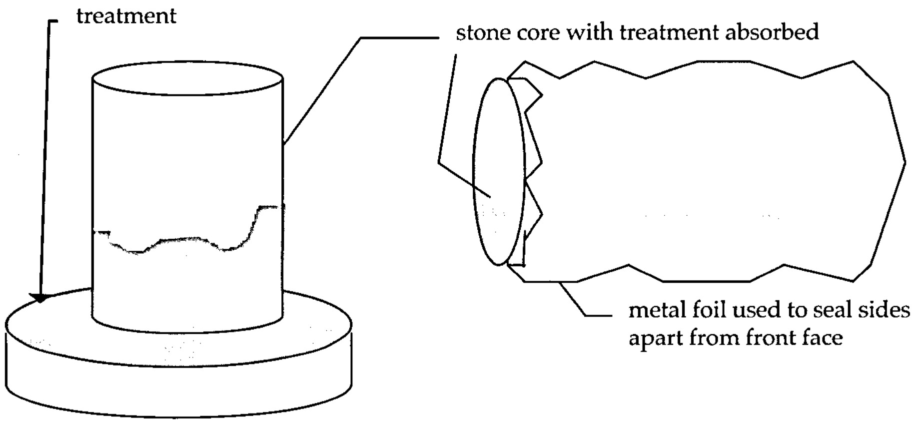


Figure 11 Treatment of cores and preparation for weight loss.

3.3.9.2 Volatile organic compounds (VOCs)

The loss of material observed in weight loss experiments could be produced by evaporation of a range of organic compounds comprising: solvents, monomers, partially polymerised monomers, condensation reaction products and water. These compounds can be described as volatile organic compounds (VOCs). To determine the exact identification and nature of VOCs evaporating from the consolidants and water repellents, gas chromatography and mass spectrometry was used. Gas chromatography (GC) allows chromatographic separation of VOCs and comparison against libraries of known VOCs for identification. Mass spectrometry (MS) provides further identification of molecules and elements to help confirm results from GC.

Experimental procedure

Samples were treated and prepared in foil as detailed previously for weight loss experiments. For analysis the samples were placed in the special chamber that collects the evaporated solvents for short periods of time for analysis (Figure 12). A known flow rate of air through the chamber passed solvents through to a GC and MS apparatus via an intermediary absorption substrate. The results can be interpreted by library search, diagnosis of mass spectrometry data, and cross-referencing of the data. Weight losses were also taken to estimate the total solvent loss as stated in Section 3.3.9.

3.3.9.3 Total weight loss (RGU methodology)

Prisms (approx. 50 x 50 x 15 mm) of Locharbriggs sandstone, lime mortar (2:5 lime:sand) and cement lime mortars (1:1:6 and 1:3:12 - cement:lime:sand) were used. The mortar prisms were cut from 7 year old mortar cubes, 10 cm square. The prisms were treated with white spirit, toluene, Con. B, Water Rep./Con. C and Water Rep. D. Samples were weighed before treatment. Samples were immersed to 1/3 of their height in each solvent/consolidant/water repellent with the original outside edge of the mortar facing downwards so that the treatment would soak up the prisms to approx. 2/3 of its height. The sandstone samples were immersed with their bedding plane vertical to simulate soaking in along the bedding planes as should happen on treatment of a correctly bedded sandstone on a building facade.

Three replicates for each stone/mortar type were made. The time allowed for treatment penetration was 60 to 120 seconds. Once treatment was complete, the samples were wrapped in aluminium foil that was held in place with adhesive tape, leaving the outside edge open to the air. The samples were weighed two hourly during the day for the first week, then daily for the following weeks until a constant weight was achieved.

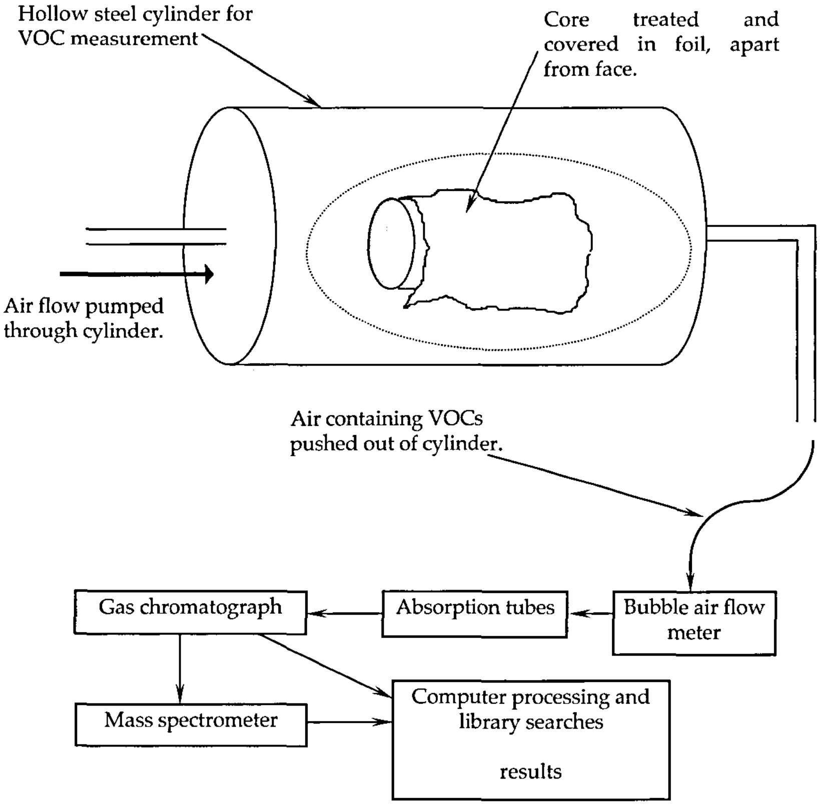


Figure 12 Diagram of basic structure of VOC apparatus and analysis.

3.3.10 Mercury porosimetry

The porosimeter used in these experiments was a Micromeritics PoreSizer 9320. This is capable of measuring pore diameters between about 0.006μm and 350μm (200 to 0.003 MPa (30000 and 0.5 psi) respectively). Mercury porosimetry can be used to measure both the effective pore volume of a sample and its pore size distribution (although the actual pore sizes measured are pore entrance sizes rather than the internal diameters of the pores). It works by intruding mercury into a stone sample under vacuum. The pressure required to force mercury into the pores is proportional to their entrance diameter. Intrusion pressure is converted to equivalent pore sizes by the Washburn equation.

$$d = - \o y \cos\theta / p \qquad \textbf{Washburn equation}$$

where,

d = width of intruded pores,

$\o$ = a shape factor. Equal to 4 for circular pore cross-sections and reducing in value to 2 for parallel walls,

y = the surface tension of mercury,

θ = contact angle between mercury and pore walls, and

p = pressure at which a given increment of mercury intrudes into the pore system.

A number of correction factors are applied to this equation. The contact angle (θ) is affected by the properties of the sample material, the drying method and the purity of the mercury. A value for the mercury contact angle of 140° has been used in the experiments described here. Other corrections are applied for any difference in pressure between the centre of the sample and the pressure gauge, surface tension changes with pore size, pore shape, machine expansion and both sample and mercury compression.

3.3.11 Analysis of residues from chemical cleaning

Samples were taken by drilling into the stone surface with a 5.5 mm masonry drill bit. Powder was collected at 0-2, 2-5, 5-10, 10-15 and 15-20 mm depths. Collection of the powdered sample was by means of a vacuum system with filters for sample retention. The vacuum system was sealed around the area to be drilled with removable adhesive.

Soluble salts were dissolved by shaking 0.1g ±0.0005g powdered sample per 100 mLs deionised water in a sealed container for one hour. The resulting solutions were suction filtered through 0.45 μm cellulose nitrate membrane filters to remove solid particles.

The ions analysed were sodium (Na^+), chloride (Cl^-), fluoride (F^-), sulphate (SO_4^{2-}), nitrate (NO_3^-) and phosphate (PO_4^{3-}). Analysis of soluble Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} was by ion chromatography, using sodium carbonate/sodium hydrogen carbonate eluent and standards of 0-20 ppm. Analysis of soluble Na^+ was by atomic absorption and analysis of soluble F^- was by ion selective electrode.

3.3.12 Measurement of mortar carbonation depth

A solution of 1% phenolphthalein in 70% ethyl alcohol was used to determine the depth of carbonation (RILEM 1994) of mortar cubes taken from mature mortar panels. Phenolphthalein is a pH indicator that gives a pink coloration on contact with alkalis and remains colourless on contact with acids. When a solution is applied to mortar it indicates carbonation depth as a clear zone surrounding a pink, non-carbonated centre.

Newly cut slices from the mortar cubes were treated by wetting with phenolphthalein solution and allowing time for the colour change to take place before photographing the samples.

3.3.13 Tomography and electrical impedance

Tomography analysis of certain properties of stone such as impedance, speed of sound, transmission of electromagnetic radiation can develop non-destructive observations of the location of consolidants and water repellents. Tomography for this purpose is a mathematical method of developing a structural model where only limited two or three dimensional peripheral data is available, essentially it guesses what is likely to be inside a closed box. At BRE it is possible to use impedance tomography on samples of stone several centimetres across. This is because the surface treatments that coat the surface of the porous structure and could act as a capacitor, or have electrical properties different from the stone.

Experimental procedure

A core of dimensions 4.5 cm diameter and 11 cm long was selected from the treated panels. A series of measurements were taken with impedance plates of 3 x 3 cm square using the range 20 Hz to 1 MHz. Measurements are also taken at different positions round the core as well as distances from the treated surface. Dielectric constants and capacitances for frequencies of 10, 100, 500 and 1000 Hz were calculated. From the impedance arcs, the timing constant t_0 can be calculated which adequately discriminates the consolidant.

Salts may cause errors in the results. However as the test is non-destructive (to the core) it could be possible to either add or leach out salts to determine the extent of the salt effect.

4 EXPERIMENTAL RESULTS

4.1 Sandstone test panels

4.1.1 RGU test panels (Aberdeen)

Figures 13(a-i) shows the test panels at The Robert Gordon University (RGU) before and after application of consolidants and water repellents. Figures 14(a-e) identify the different sandstones in the test panels.

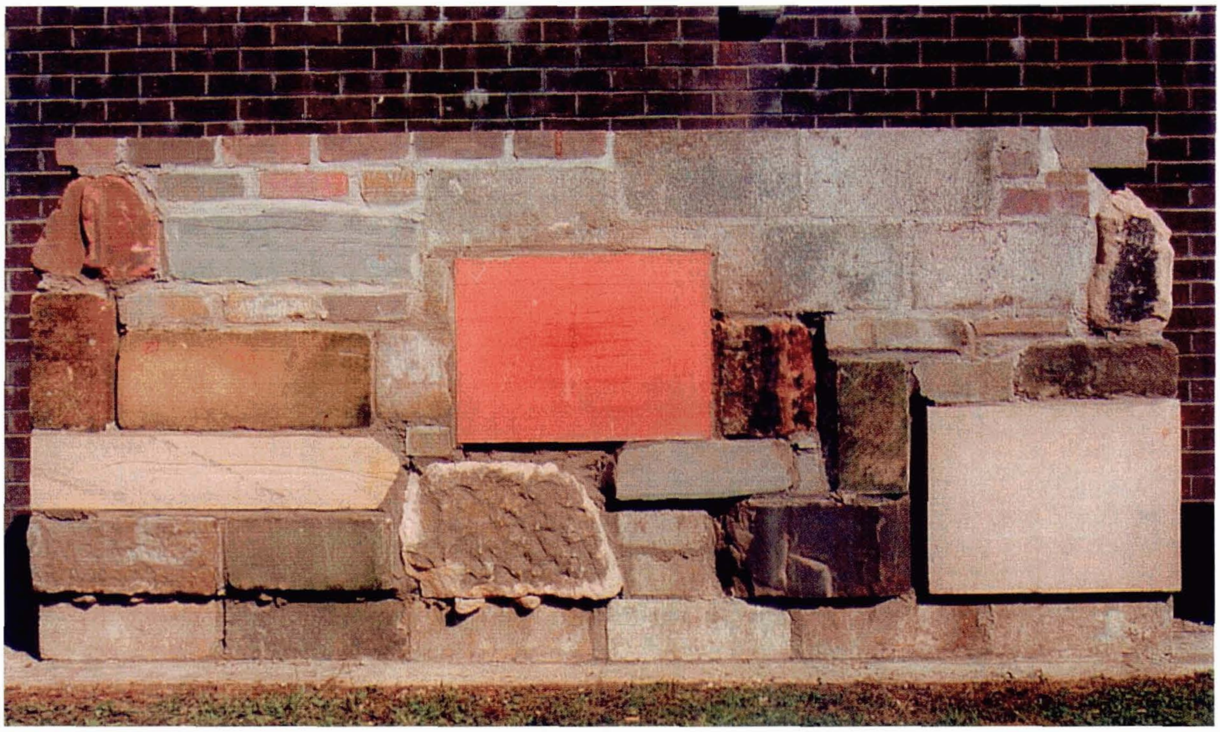


Figure 13a RGU Panel 1. Control - no treatment.

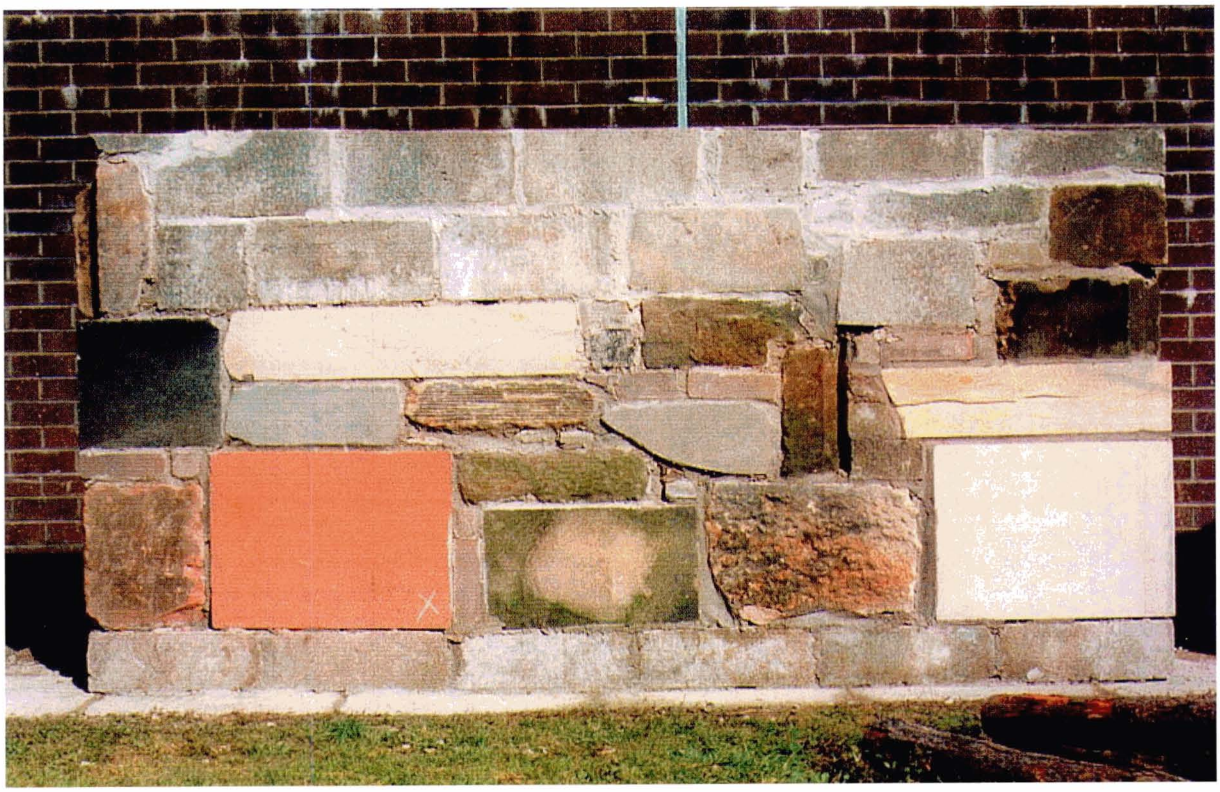


Figure 13b RGU Panel 2. Before treatment.

Figure 13c RGU Panel 2. Treated with Consolidant A.

Figure 13d RGU Panel 3. Before treatment.

Figure 13e RGU Panel 3. Treated with Water Rep./Con. C.

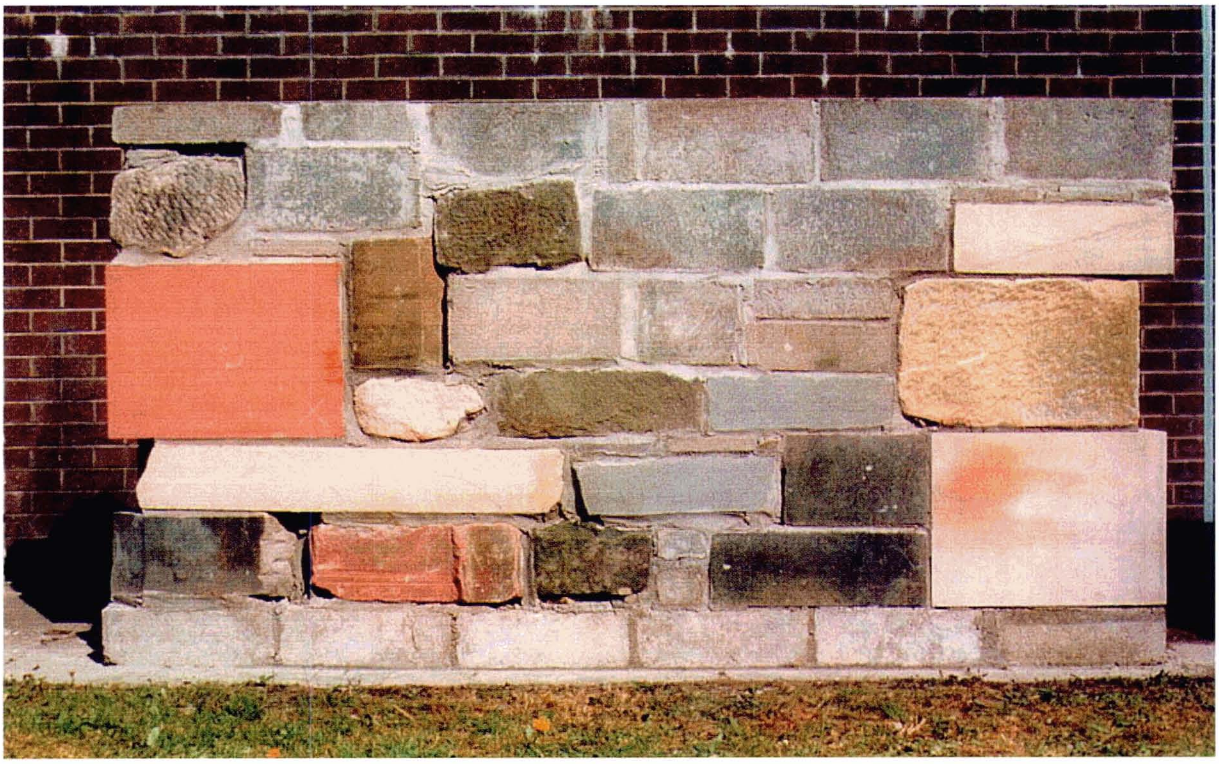


Figure 13f RGU Panel 4. Before treatment.

Figure 13g RGU Panel 4. Treated with Water Repellent D.

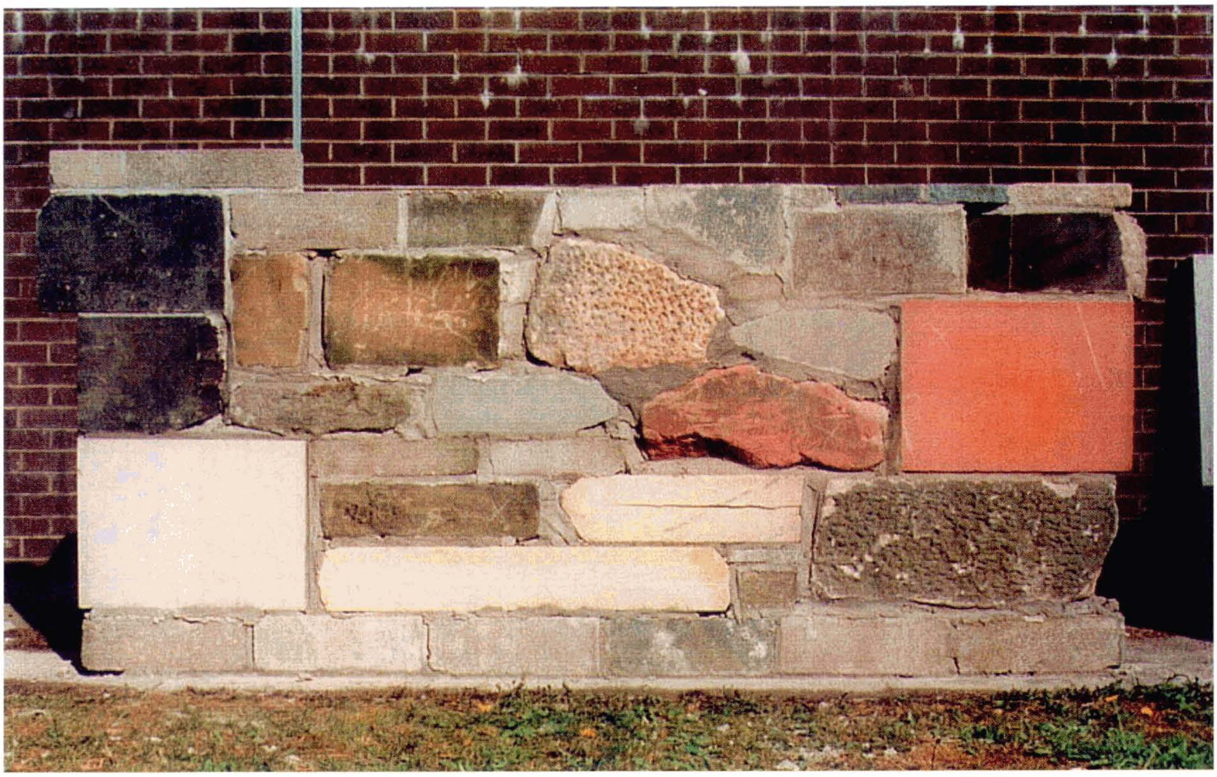


Figure 13h RGU Panel 5. Before treatment.

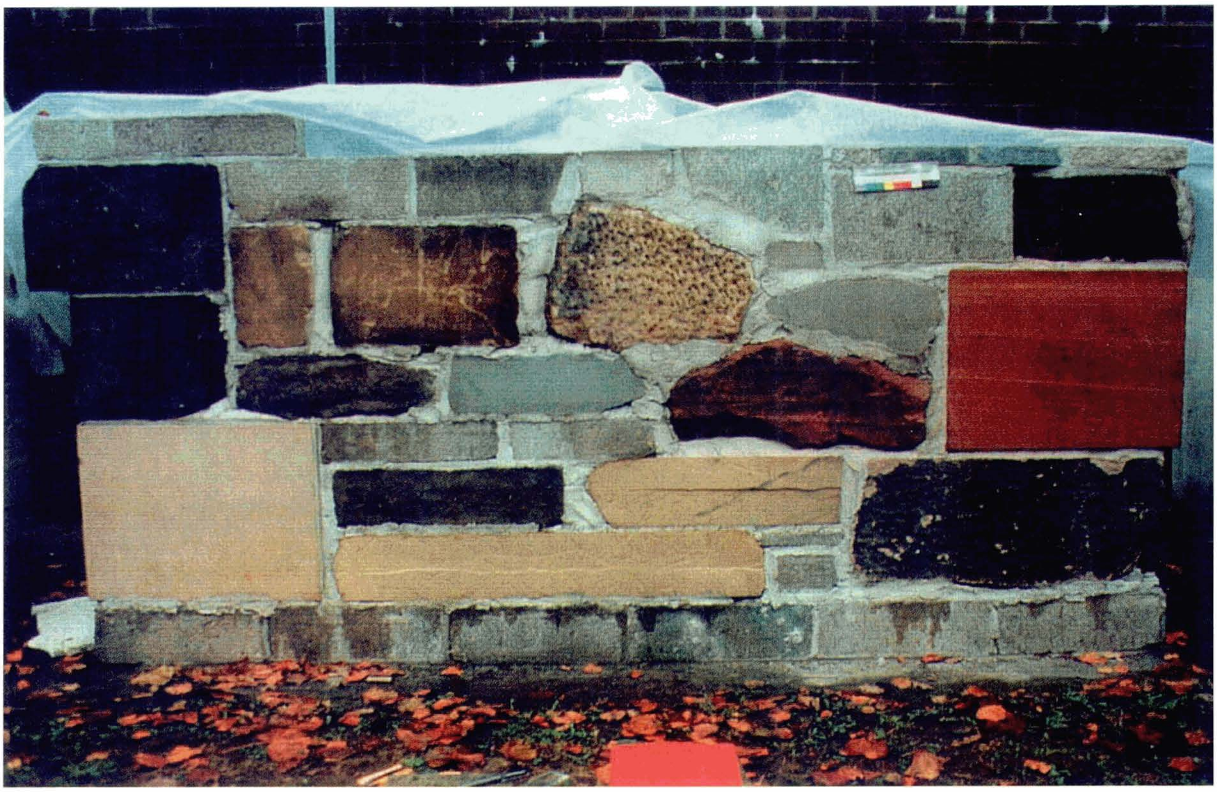


Figure 13i RGU Panel 5. Treated with Consolidant B.

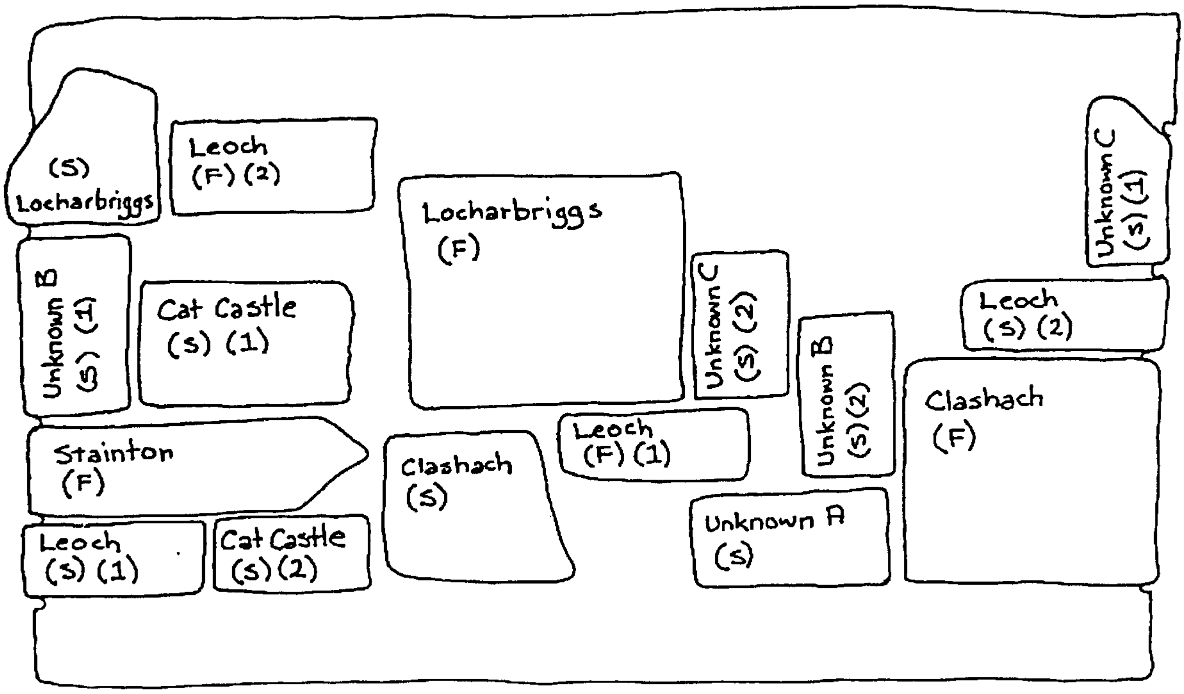


Figure 14a Diagram identifying the different sandstones used in Panel 1.
(F): fresh, (S): soiled, (1): where more than one sandstone of the same type has been used.

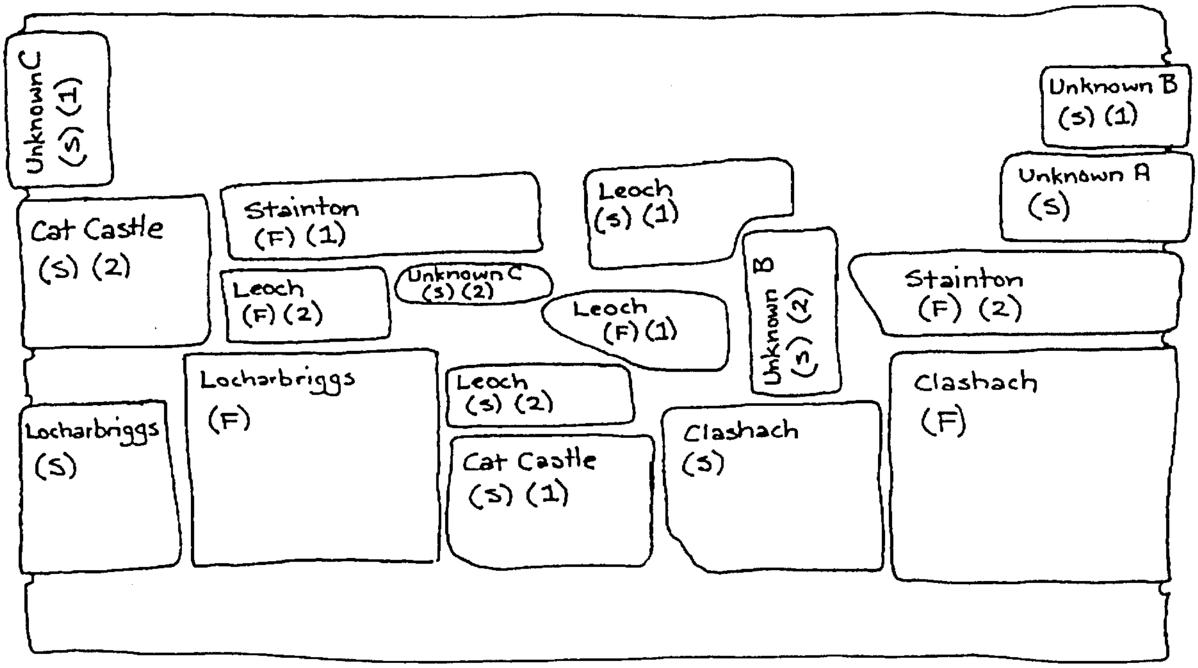


Figure 14b Diagram identifying the different sandstones used in Panel 2.
(F): fresh, (S): soiled, (1): where more than one sandstone of the same type has been used.

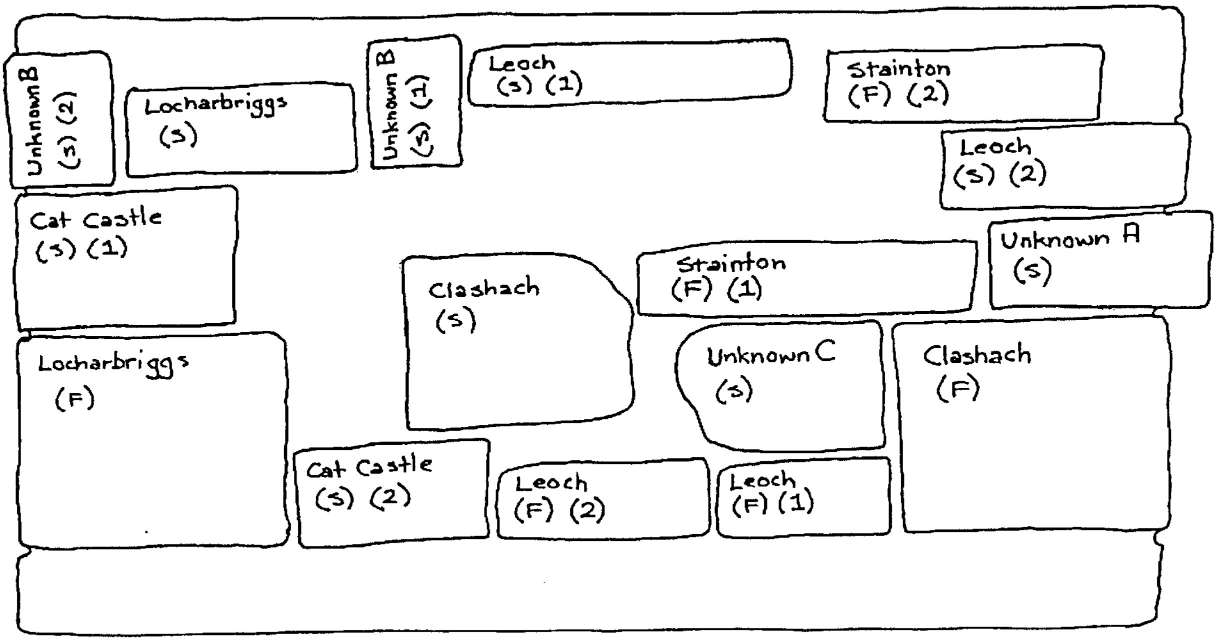


Figure 14c Diagram identifying the different sandstones used in Panel 3.
(F): fresh, (S): soiled, (1): where more than one sandstone of the same type has been used.

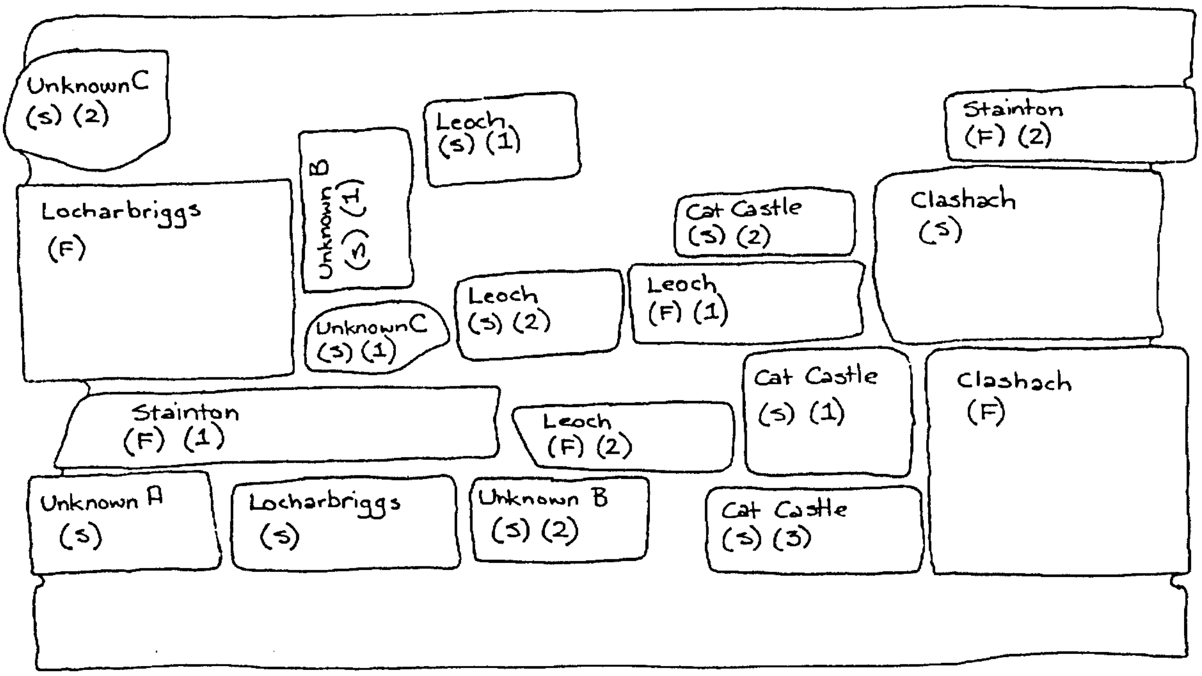


Figure 14d Diagram identifying the different sandstones used in Panel 4.
(F): fresh, (S): soiled, (1): where more than one sandstone of the same type has been used.

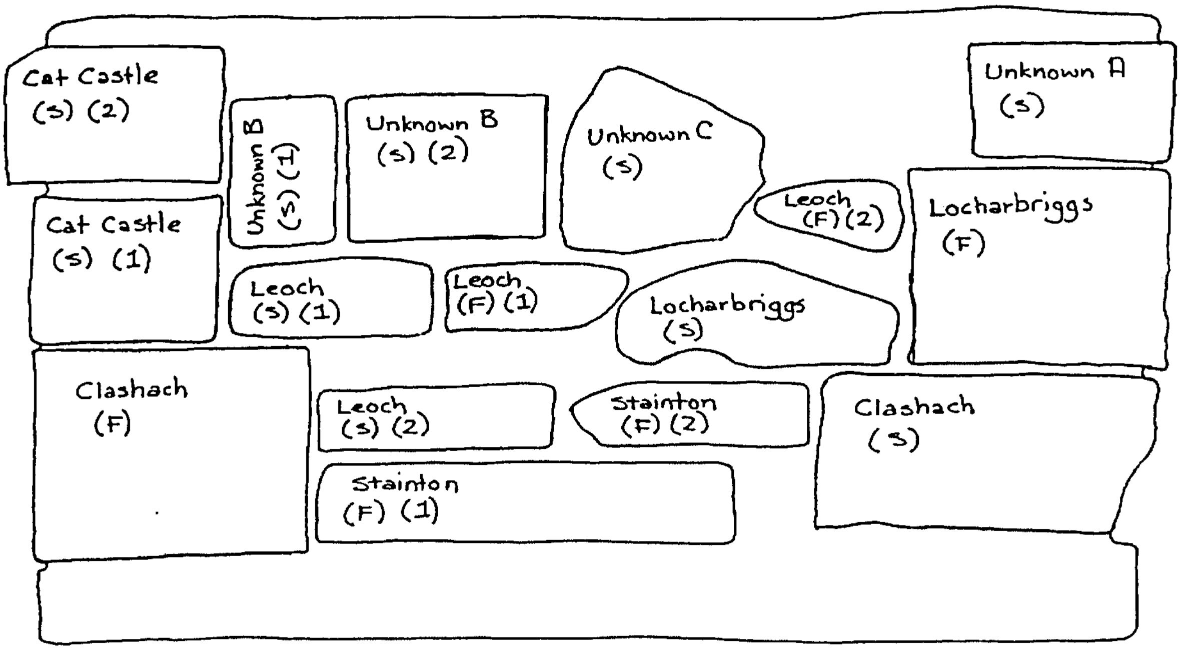


Figure 14e Diagram identifying the different sandstones used in Panel 5.
(F): fresh, (S): soiled, (1): where more than one sandstone of the same type has been used.

4.1.2 BRE test panels (Myers Hill)

Natural weathering of treated sandstone was carried out at Myers Hill (altitude 300m), the BRE exposure site near East Kilbride, Glasgow. Consolidant A, Consolidant B (10% and 30% solution in toluene), Water Rep./Con. C and Water Repellent D were used as treatments applied to test panels of sandstones.

Two panels were built to a specification similar to the panels at the RGU site using 1:2:9 (cement : lime : sand) mortar mix (Figure 15). The panels were recorded as Panel 1 and Panel 2. A range of sandstone types were used which were classed as soiled or fresh (Figure 16). The panels were left to dry and covered in plastic to await treatment. Before treatment the plastic was removed and any residual dampness left to dry.

Consolidant B and Water Repellent D treatment

The application of Water Repellent D and Consolidant B was carried out on October 1996 by Nick Boyce of Historic Scotland's Stenhouse Conservation Centre and Matthew Murray (BRE). The weather was dry and the temperature was 11°C. Each block of stone was divided into zones to specify the location of each treatment. On Panel 1 treatments were applied of 10% Consolidant B in toluene supplied by RGU, and 30% Consolidant B in toluene supplied by Nick Boyce (Figure 17). One area was left untreated. The pure solvent (toluene) was used to rinse away surface residues. On Panel 2 Water Repellent D was applied using white spirit to rinse the surface (Figure 18). The panels were covered in plastic sheets for two weeks after treatment for curing.

Consolidant A and Water Repellent / Consolidant C treatment

Consolidant A and Water Rep./Con. C were applied to Panel 2 by Matthew Murray in November 1996 (Figure 18). The weather was dry, the temperature was 3°C, and there was several inches of snow on the ground (panel covers had been used to stop snow or rain wetting). Some treatment spilled onto other areas of stonework, which was noted on maps of the panel. After application the panels were sealed with foil, and then covered in plastic sheeting. The weather conditions were outside the product suppliers instructions as the temperature should be above 10°C. However the time scale of the project did not allow a delay to the next summer.

The panels were photographed at 6 and 12 months in dry conditions over a period of one year. The photographs are shown in Figures 19 to 20. Visual observation and inspection of photographs was used to assess any changes to the panels.

Quality and consistency of photography and visual observation will vary because of weather conditions, development methods, film and camera type; however, qualitative differences between the treatments were observed due to application and weather changes.

Consolidant B treatment

There was an initial visible change due to the treatment application. This was characterised as an intensification of the colours and a darkening effect. 10 out of the 11 stone samples showed an appearance difference. There were some differences over time which were not consistent. Photography in May showed white patchy appearances on all the treated areas.

Consolidant A, Water Rep./Con. C, Water Repellent D treatments

The Consolidant A, Water Rep./Con. C and Water Repellent D treatments did not show any consistent long-term changes in appearance. Although photographs in May show patchy water effects similar to those on the Consolidant B panel.

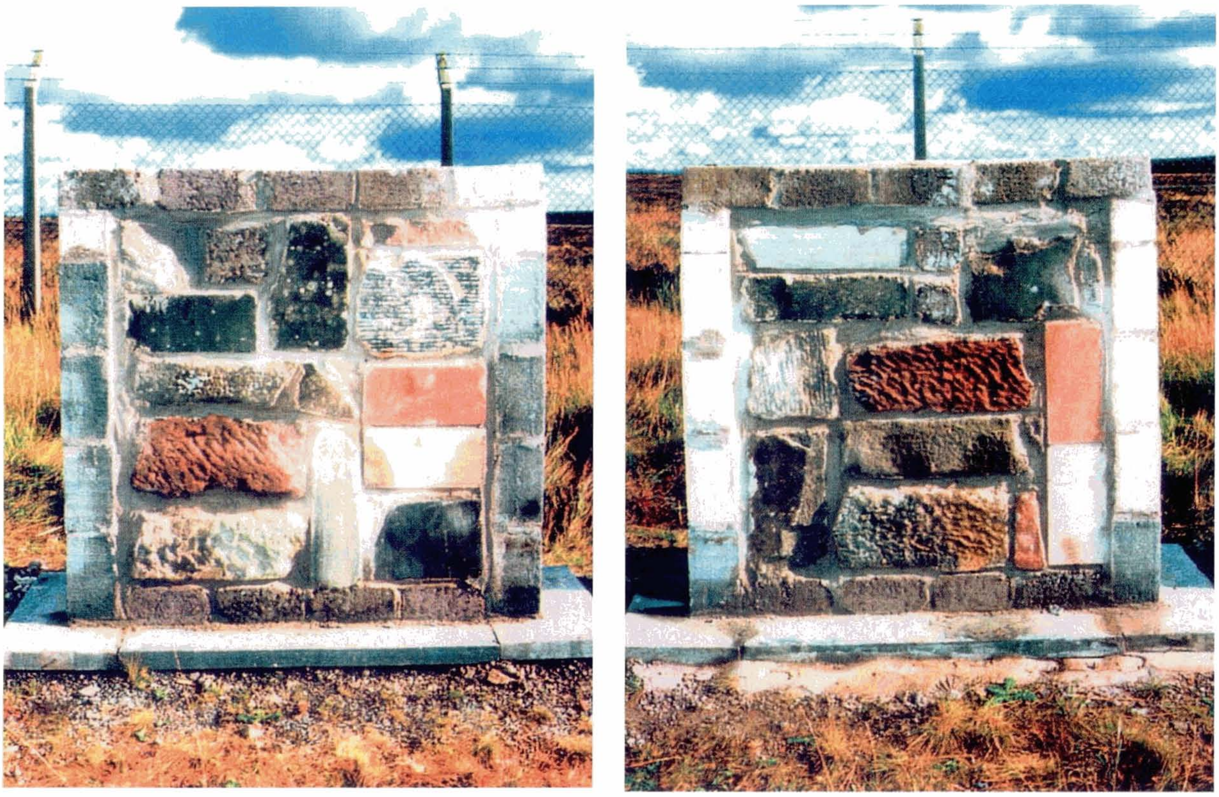
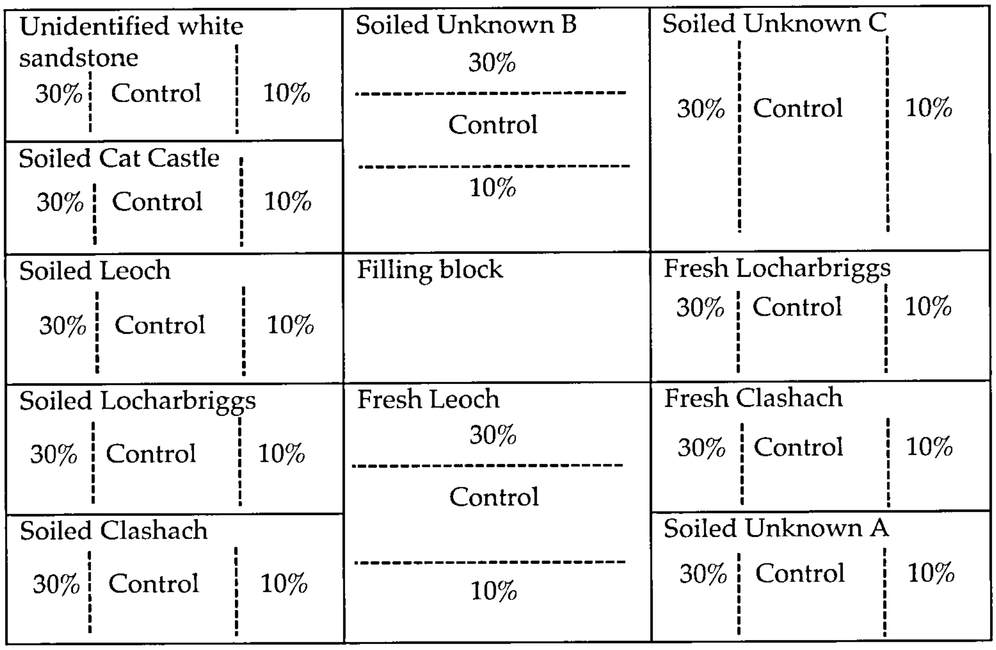
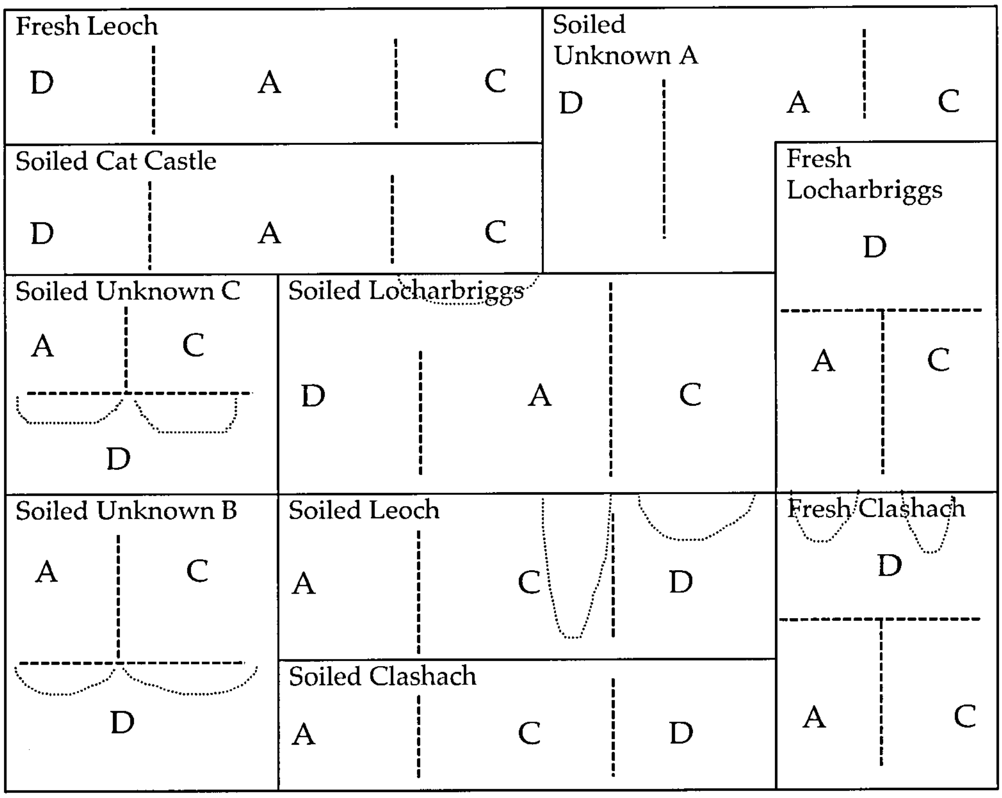


Figure 15 Panels before treatment (Panel 1 left, Panel 2 right).



Panel 1 *Location of treatments with Consolidant B mixes.*



Panel 2 *Treatment locations of Consolidant A (A), Water Rep./Con. C (C), and Water Repellent D (D). The dotted marks denote where treatments spilled into other areas.*

Figure 16 Diagram of test panels used for exposure of treatments at Myers Hill, East Kilbride.

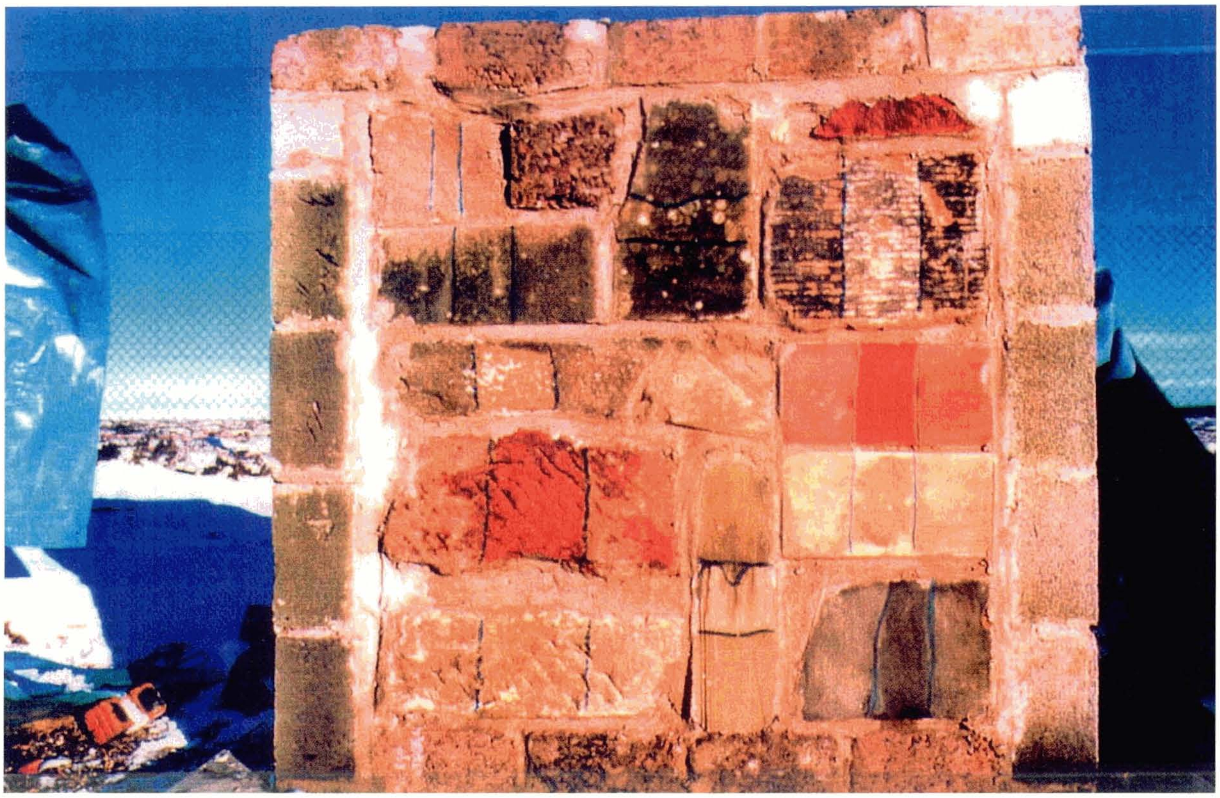


Figure 17 Panel 1 Two weeks after treatment (Consolidant B).

Figure 18 Panel 2 Immediately after treatment (Consolidant A, Water Rep./Con. C, Water Repellent D).

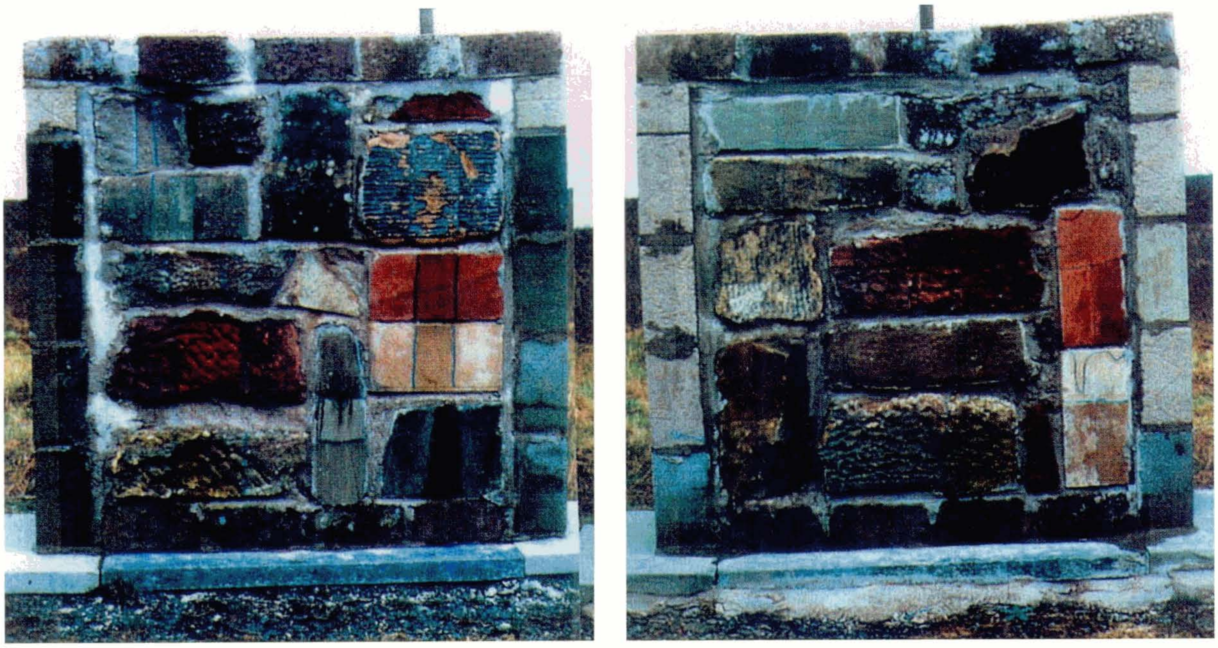


Figure 19 *Panels after 6 months exposure (Panel 1 left, Panel 2 right).*

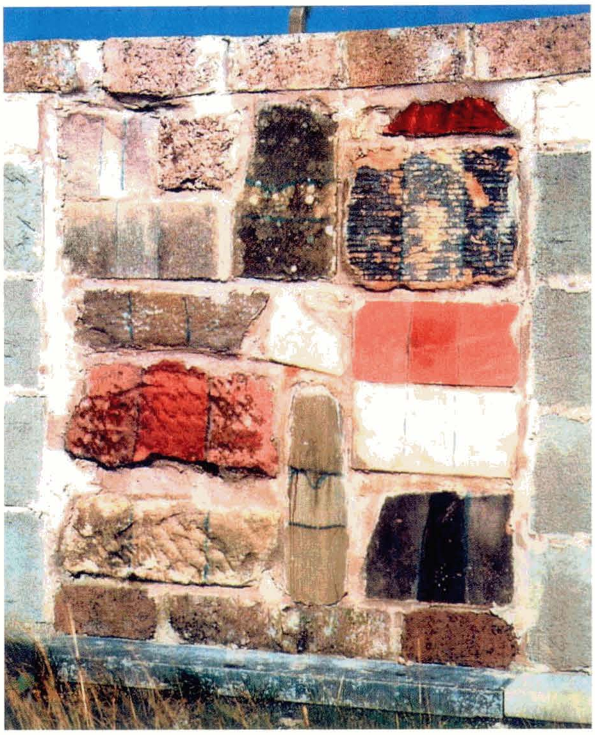


Figure 20 *Panel 1 after one year's exposure.*

Figure 21 *Panel 2 after one year's exposure.*

4.2 Amounts of consolidants and water repellents applied to sandstones

4.2.1 RGU test panels

The amount of consolidants or water repellent applied to each sandstone block (Figure 22 and Table 4) in the test panels at RGU was calculated by weighing the amount of material used during application and measuring the surface area of each stone. Surface areas of blocks were calculated either by measuring the lengths of the sides (on square cut blocks) or by tracing the block and cutting out and weighing a paper outline of each block (for irregular blocks).

There were wide variations in the amounts of consolidants and water repellents taken up by the sandstones. Amounts absorbed ranged from 173 g/m^2 for fresh Leoch sandstone to 3267 g/m^2 for fresh Locharbriggs sandstone. The data in Table 4 show the total amount of consolidant or water repellent applied to the sandstone, the actual amount remaining in the sandstone after treatment will be smaller if there has been any run-off from the surface (application was carried out carefully to minimise this, but some run-off was inevitable) or if any consolidant has been removed during wash-off of the surface with solvent. Later results indicated that where solvent wash-down was used in the last stage of treatment, this did appear to remove some of the treatment from the outer few millimetres of the sandstone with a resulting reduction in strength (Section 4.4.3). All the panels, with the exception of Panel 4, treated with Water Repellent D, were washed down with solvent after application of the treatment. The intention in this final wash-down is to reduce surface colour changes caused by excess treatment polymerising on the immediate surface.

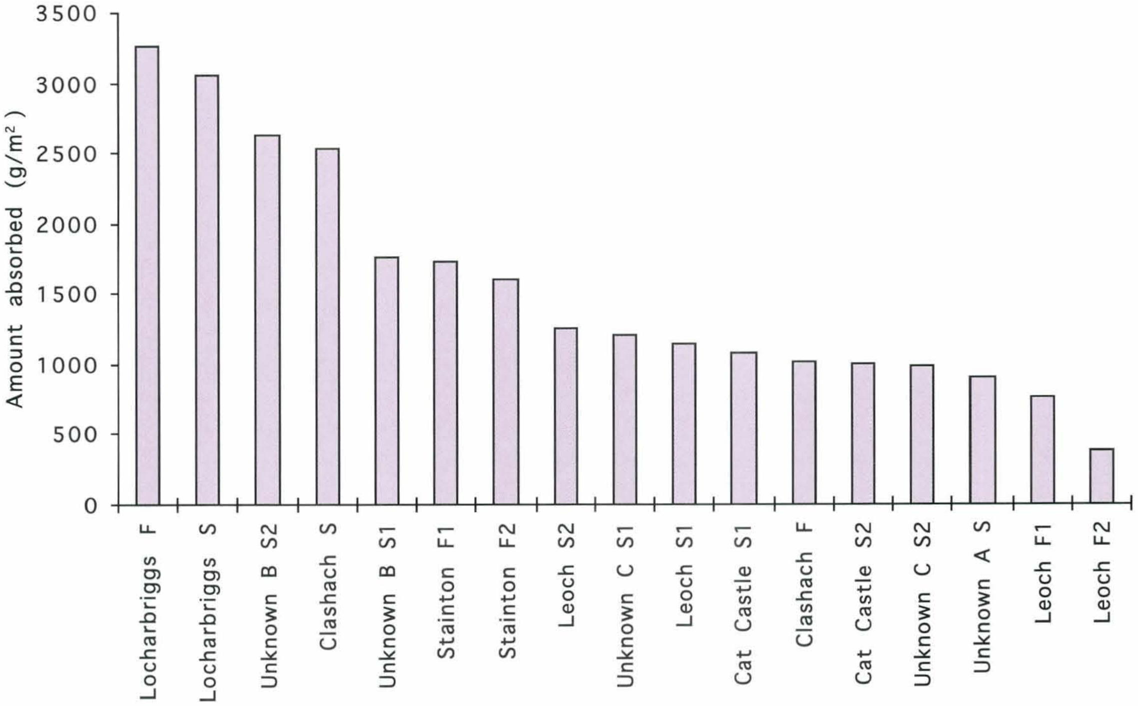


Figure 22a Panel 2. Amount (in g/m²) of Consolidant A taken up by sandstone samples. F: fresh, S: soiled, 1 or 2: sample 1 or 2.

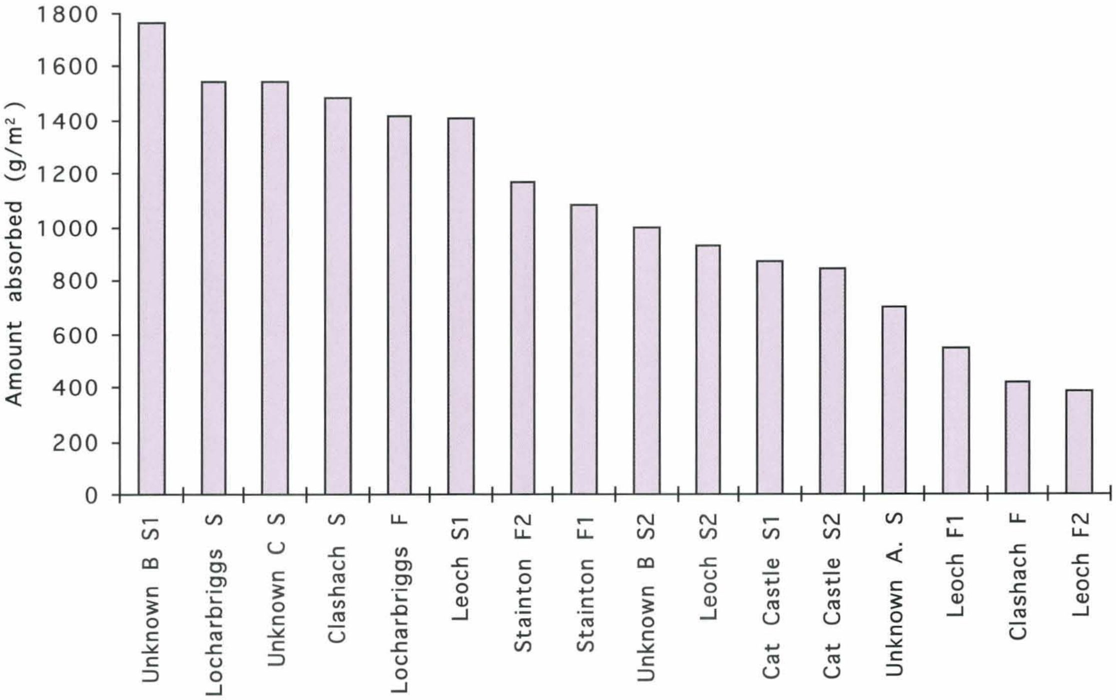


Figure 22b Panel 5. Amount (in g/m²) of Consolidant B taken up by sandstone samples. F: fresh, S: soiled, 1 or 2: sample 1 or 2.

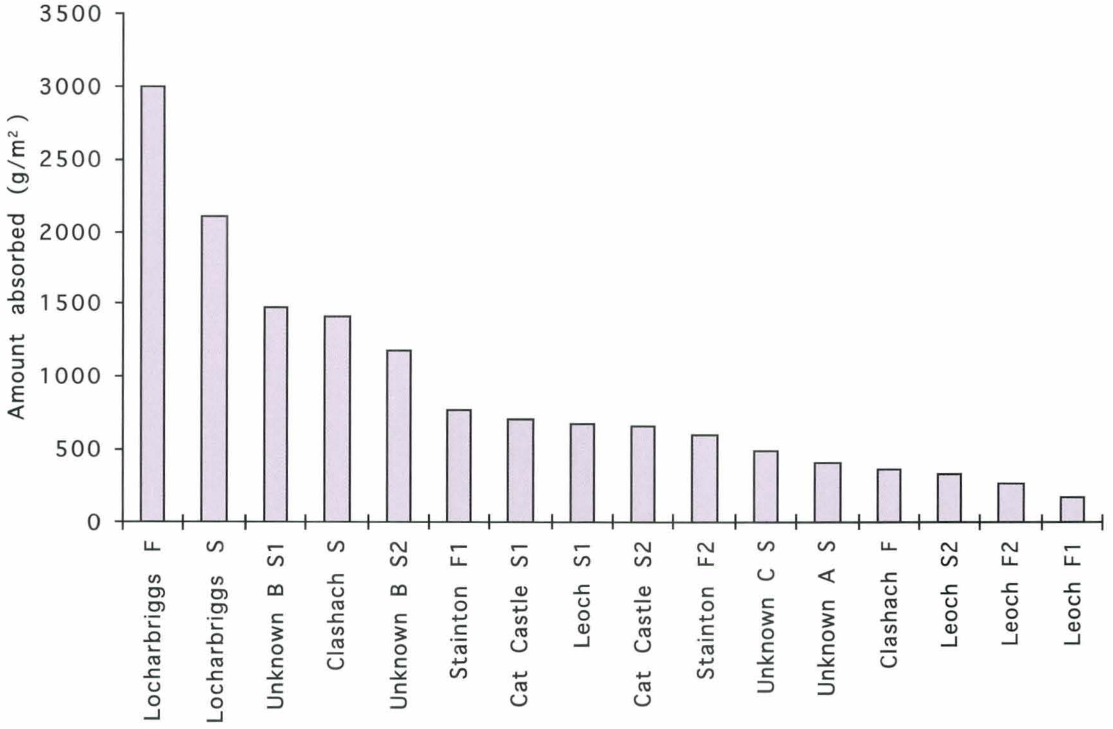


Figure 22c *Panel 3. Amount (in g/m²) of Water Rep./Con. C taken up by sandstone samples. F: fresh, S: soiled, 1 or 2: sample 1 or 2.*

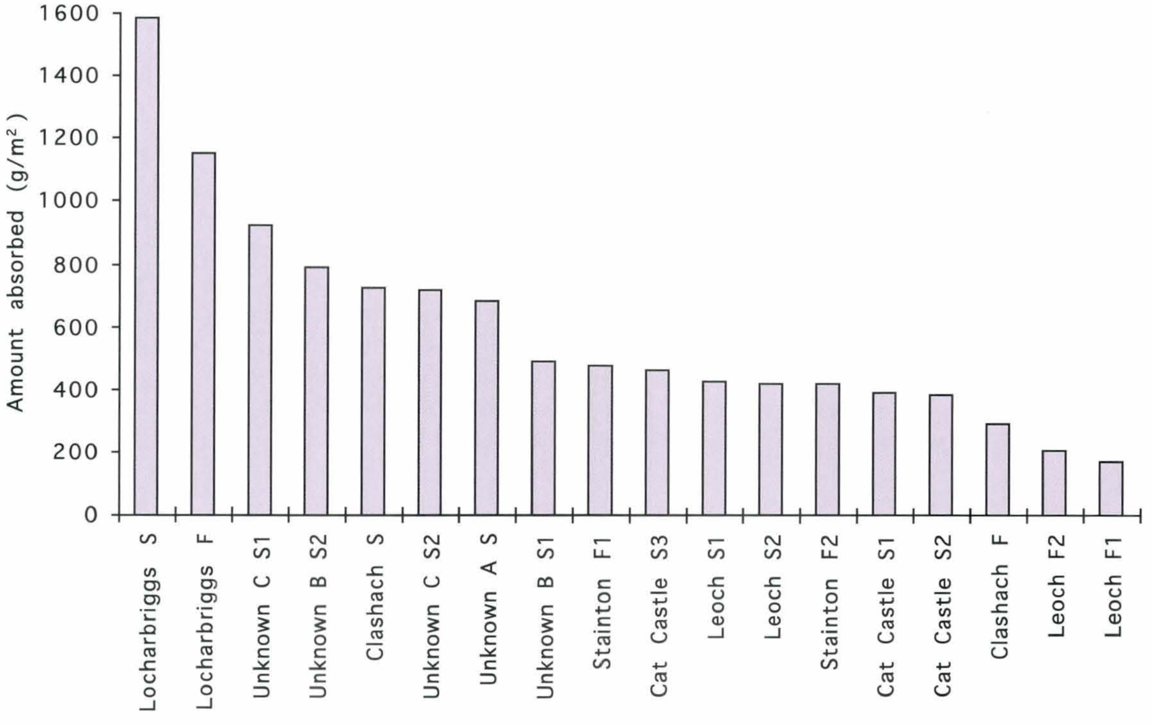


Figure 22d *Panel 4. Amount (in g/m²) of Water Repellent D taken up by sandstone samples. F: fresh, S: soiled, 1 or 2: sample 1 or 2.*

	Amount applied (g/m²)			
Sandstone	**Panel 2**	**Panel 3**	**Panel 4**	**Panel 5**
Locharbriggs fresh	3267	3002	1151	1412
Locharbriggs soiled	3057	2097	1588	1547
Clashach fresh	1016	360	290	422
Clashach soiled	2532	1416	727	1487
Stainton fresh (1)	1725	770	475	1082
Stainton fresh (2)	1596	590	417	1170
Unknown B soiled (1)	1758	1469	487	1764
Unknown B soiled (2)	2626	1185	787	1001
Leoch fresh (1)	752	176	173	542
Leoch fresh (2)	383	274	204	383
Leoch soiled (1)	1145	673	428	1411
Leoch soiled (2)	1258	337	420	927
Cat Castle soiled (1)	1069	712	391	872
Cat Castle soiled (2)	1000	662	386	847
Cat Castle soiled (3)	ns	ns	464	ns
Unknown A soiled	904	404	682	702
Unknown C soiled (1)	1209	488	924	1540
Unknown C soiled (2)	978	ns	721	ns

ns: no sample

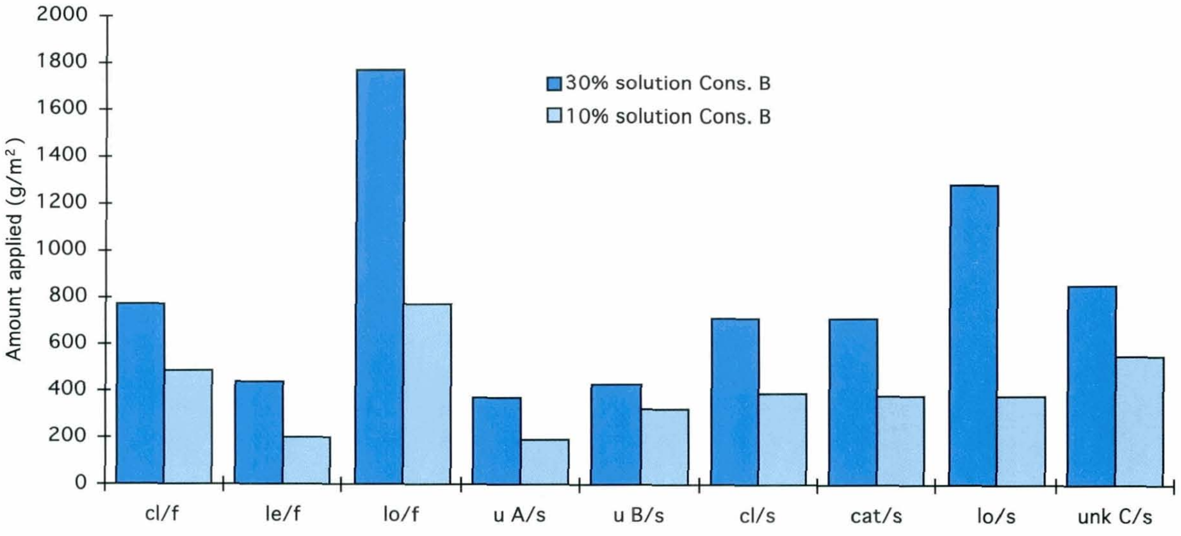
Table 4 Amounts of consolidants or water repellent applied to each sandstone block.

Overall, the most absorbent sandstone type was found to be Locharbriggs sandstone which could absorb up to about 20 times as much consolidant/water repellent as the least absorbent sandstone type (Leoch sandstone). In the case of Leoch sandstone it was noticeable that the soiled, weathered samples were able to take up substantially more consolidant than the fresh sandstone (the fresh samples of Leoch were cut from the interior of weathered blocks, so the stone itself is identical in the soiled and fresh form). This effect was caused by increased porosity (Section 4.4.10) in the weathered sandstone, some of which was in the form of surface parallel cracks. It was generally, but not consistently, the case that where weathered and fresh samples of similar sandstones could be compared, the weathered sandstone absorbed more consolidant/water repellent than the fresh sandstone. These results would be consistent with the expectation that weathering increases the permeability of the outer layers of the sandstone and this was confirmed by results of porosimetry (Section 4.4.10).

4.2.2 BRE test panels

The application of Consolidant B and Water Repellent D to the panels at Myers Hill was monitored by weighing the amount of consolidant before and after one application. Two dilutions of Consolidant B were used, 10% in toluene supplied by RGU and 30% in toluene supplied by a Historic Scotland conservator. The area of the stone surface was recorded to determine the grams applied per square meter. Unfortunately weather and time constraints did not allow measurement of the application of other treatments. Figure 23 shows the volume of treatments applied to the panels. The stone types are summarised:

Cl=Clashach, Le=Leoch, Lo=Locharbriggs, UA=Unknown A, UB=Unknown B, Cat=Cat Castle, UC=Unknown C. F=fresh, S=soiled.



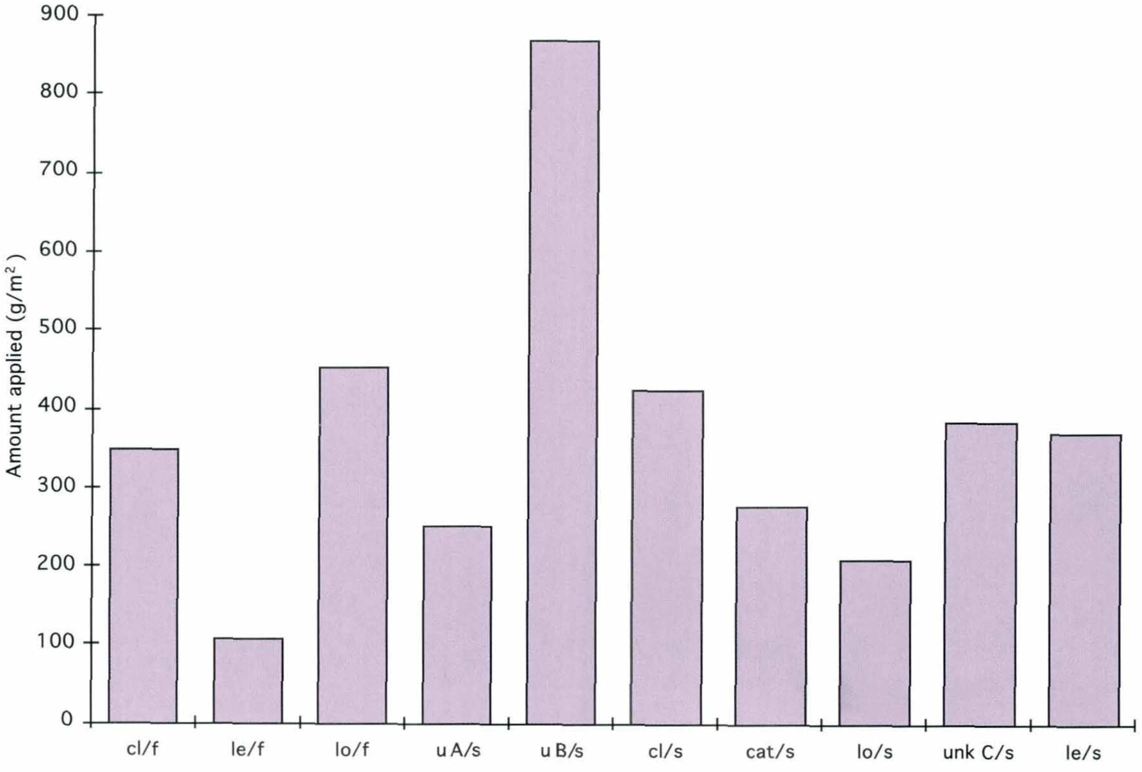


Figure 23 *Volume of treatments applied to the panels. Above Consolidant B, below Water Repellent D.*

Consolidant B (10% and 30% concentration)

The results for application of Consolidant B were broadly consistent with work at RGU in applying consolidants to sandstone panels: the more porous stones such as Locharbriggs absorbed more treatment. The thicker 30% concentration allowed longer retention on the surface, and so allowed more absorption of the total mix.

Water Repellent D

Water Repellent D was more difficult to apply to the surfaces. As a result, the comparisons of volumes applied to different stone types were not entirely consistent with other RGU results. Also, less caution is required with blocks that do not have a sample below and so more treatment can be applied.

4.3 Petrological examination of sandstones

The results from petrographic analysis of the sandstones used in the test panels are presented in Table 5 and diagrammatic form in Figure 24. Petrographic examination of the sandstones in thin section allows analysis of the mineralogical composition of the sandstones (Section 3.3.1).

Detrital minerals (%)										**Authigenic minerals (%)**							
Sandstone	**qtz**	**orth**	**Ksp**	**plag**	**musc**	**bio**	**rock**	**heav**	**opq**	**qtz**	**flsp**	**calc**	**dol**	**kao**	**clays**	**chlor**	**fe-ox**
Locharbriggs (f)	90	5	1	0	<<1	0	<<1	<<1	1	<<1	<<1	0	0	0	2	0	1
Locharbriggs (s)	93	3	<<1	<<1	<<1	<<1	<<1	<<1	2	2	<<1	0	0	0	<<1	0	<<1
Clashach (f)	84	5	1	<<1	<<1	0	2	<<1	<<1	5	<<1	0	0	0	3	<<1	0
Clashach [1] (s)	67	5	2	0	<<1	0	20	<<1	<<1	1	<<1	0	0	0	5	0	<<1
Clashach [2] (s)	88	10	<<1	0	<<1	0	0	<<1	0	2	<<1	0	0	0	1	0	0
Clashach [3] (s)	85	10	<<1	<<1	1	0	0	<<1	<<1	1	1	0	0	0	2	0	0
Leoch (f & s)	25	10	<<1	2	2	2	46	<<1	2	0	0	10	0	0	0	1	0
Stainton (f)	84	2	<<1	0	1	0	0	<<1	0	2	0	0	0	5	1	0	5
Cat Castle (s)	83	5	1	<<1	<<1	0	1	<<1	0	2	0	0	0	5	2	0	2
Unknown A (s)	68	5	0	<<1	1	<<1	20	<<1	<<1	2	0	0	0	1	0	2	1
Unknown B (s)	75	3	<<1	2	2	0	<<1	<<1	0	<<1	0	2	5	5	1	0	5
Unknown C[1] (s)	87	2	3	<<1	1	0	<<1	<<1	0	1	0	0	0	5	<<1	0	1
Unknown C[2] (s)	89	1	1	0	<<1	0	0	<<1	0	1	0	7	0	1	0	0	<<1

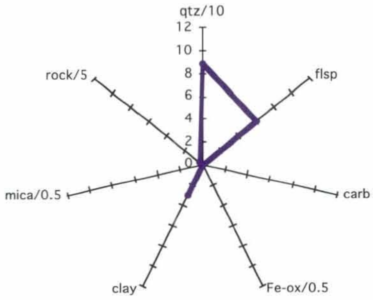
(f): fresh (s): soiled
qtz: quartz
orth: orthoclase feldspar
Ksp: potassium feldspar
plag: plagioclase feldspar
flsp: feldspar (type not defined)

musc: muscovite mica
bio: biotite mica
rock: rock fragments
heav: heavy minerals
opq: opaque minerals
calc: calcite

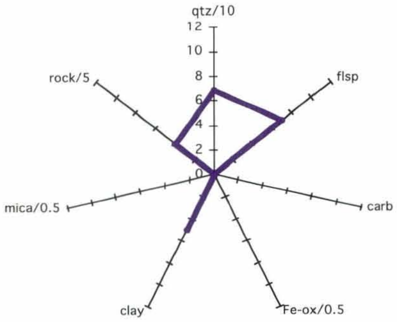
dol: dolomite
kao: kaolinite
clay: clays (not including kaolinite)
chlor: chlorite
fe-ox: iron oxides & hydroxides

Table 5 Results from petrographic analysis of sandstones. Amounts of minerals are shown as percentages. "Detrital" minerals are the "sand grains" which make up the body of the sandstone. "Authigenic" minerals are minerals deposited during the formation of the sandstone, e.g. cements. Where the sandstone showed some variation in composition a number of different sandstones were examined, e.g. Clashach [1] to [3].

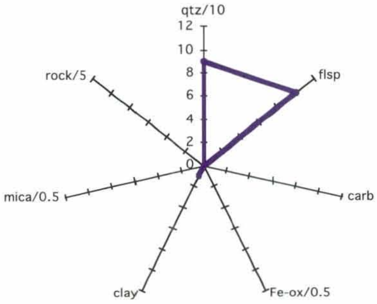
Clashach sandstone fresh



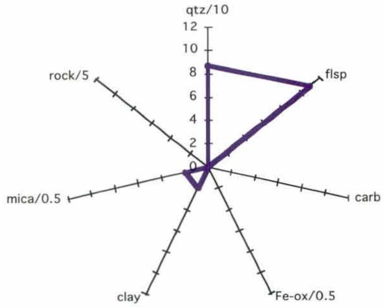
Clashach sandstone soiled (1)



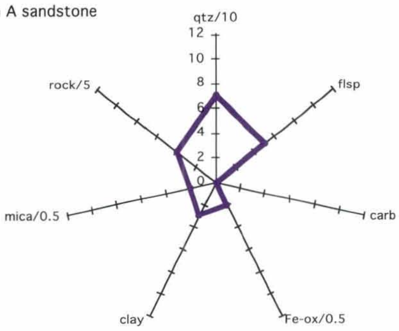
Clashach sandstone soiled (2)



Clashach sandstone soiled (3)



Unknown A sandstone



Key

qtz/10: % quartz/10

flsp: % feldspar (orthoclase + plagioclase)

carb: % carbonate (calcite + dolomite)

Fe-ox/0.5: % iron oxides + hydroxides/0.5

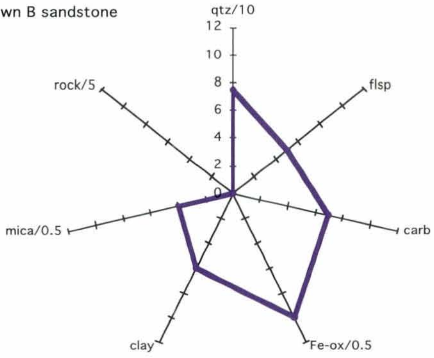
clay: % clays (e.g. kaolinite, etc.)

mica/0.5: % mica (muscovite + biotite)

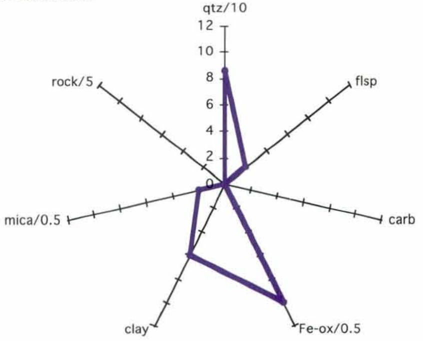
rock/5: % rock fragments (e.g. schist, etc.)

Figure 24 Graphical representation of results of petrographic analysis of sandstones from test panels.

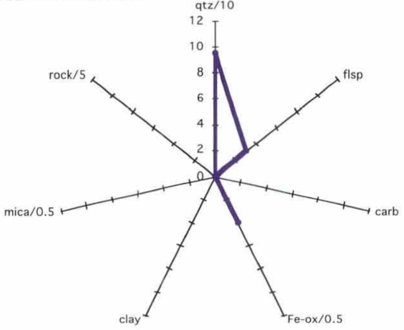
Unknown B sandstone



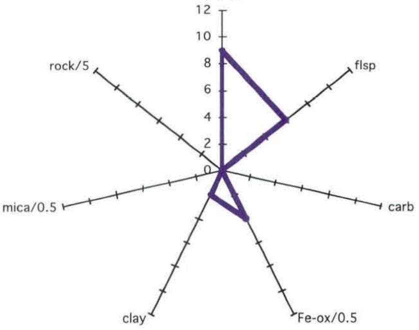
Stainton sandstone



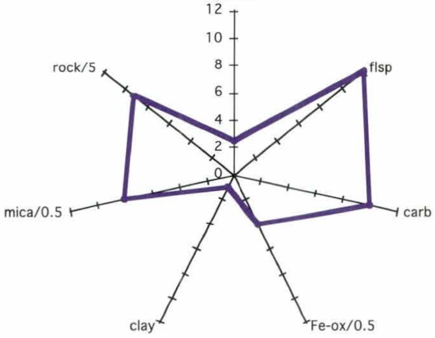
Locharbriggs sandstone soiled



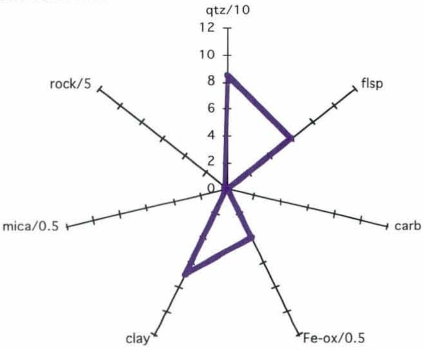
Locharbriggs sandstone fresh



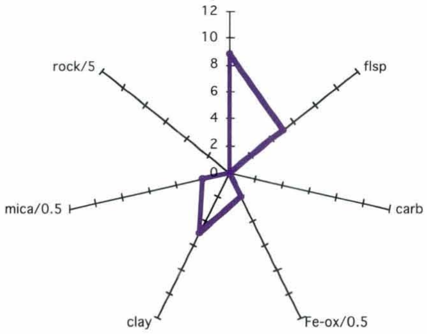
Leoch sandstone



Cat Castle sandstone



Unknown C(1) sandstone



Unknown C2 sandstone

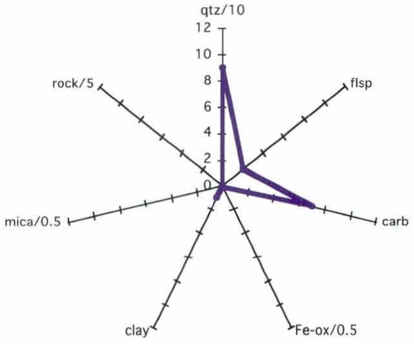


Figure 24 continued......

In later sections, comparisons have been made between the performance of consolidant and water repellent treatments on fresh and soiled sandstones. For this purpose, some sandstones from the test panels have been paired. The pairs were:

- Locharbriggs fresh with Locharbriggs soiled
- Clashach fresh with Clashach soiled
- Leoch fresh with Leoch soiled
- Stainton fresh with Unknown B soiled.

The above data show that both Locharbriggs and Clashach sandstones soiled and fresh were a good match for each other mineralogically. Leoch soiled and fresh were identical as the same stones were used to provide both surface types (the sandstone blocks being sawn in half to provide "fresh" faces). Sandstone types Unknown B (soiled) and Stainton (fresh) had some differences in their mineralogy. The Unknown B sandstone contained some dolomite ($CaMg(CO_3)_2$)and calcite ($CaCO_3$). No carbonate minerals were found in Stainton sandstone.

The sandstones used on the test panels covered a wide range of compositions. Some were highly quartz rich (Locharbriggs & Unknown C), others contained a high proportion of rock fragments (Leoch & Clashach (1)). The cements present in the sandstones also varied widely and included silica (quartz), iron oxides/hydroxides, calcite, dolomite and various clay minerals.

Sandstones can be classified into types on the basis of their mineralogy, specifically, according to their quartz, feldspar and rock fragment components, along with other descriptors based on other aspects of their mineralogy (e.g. calcareous, ferruginous, etc.). The ternary diagram used to describe the composition of the sandstones is shown in Figure 25. The quartz, feldspar and rock fragment total is normalized to 100 and the normalized amounts of all three components are then plotted on the diagram. Each vertex represents 100% of that particular component. Note that although the fresh and soiled Locharbriggs sandstones give different compositional classifications, their compositions actually plot very closely together on the diagram.

Sandstone		***Sandstone type***
Locharbriggs fresh	:	ferruginous sub arkose
Locharbriggs soiled	:	ferruginous quartz arenite
Clashach fresh	:	sub arkose
Clashach soiled [1]	:	feldspathic litharenite
Clashach soiled [2]	:	sub arkose
Clashach soiled [3]	:	sub arkose
Leoch fresh & soiled	:	calcareous litharenite
Stainton fresh	:	quartz arenite
Cat Castle soiled	:	sub arkose
Unknown A soiled	:	litharenite
Unknown B soiled	:	calcareous dolomitic sub arkose
Unknown C soiled [1]	:	quartz arenite
Unknown C soiled [2]	:	calcareous quartz arenite

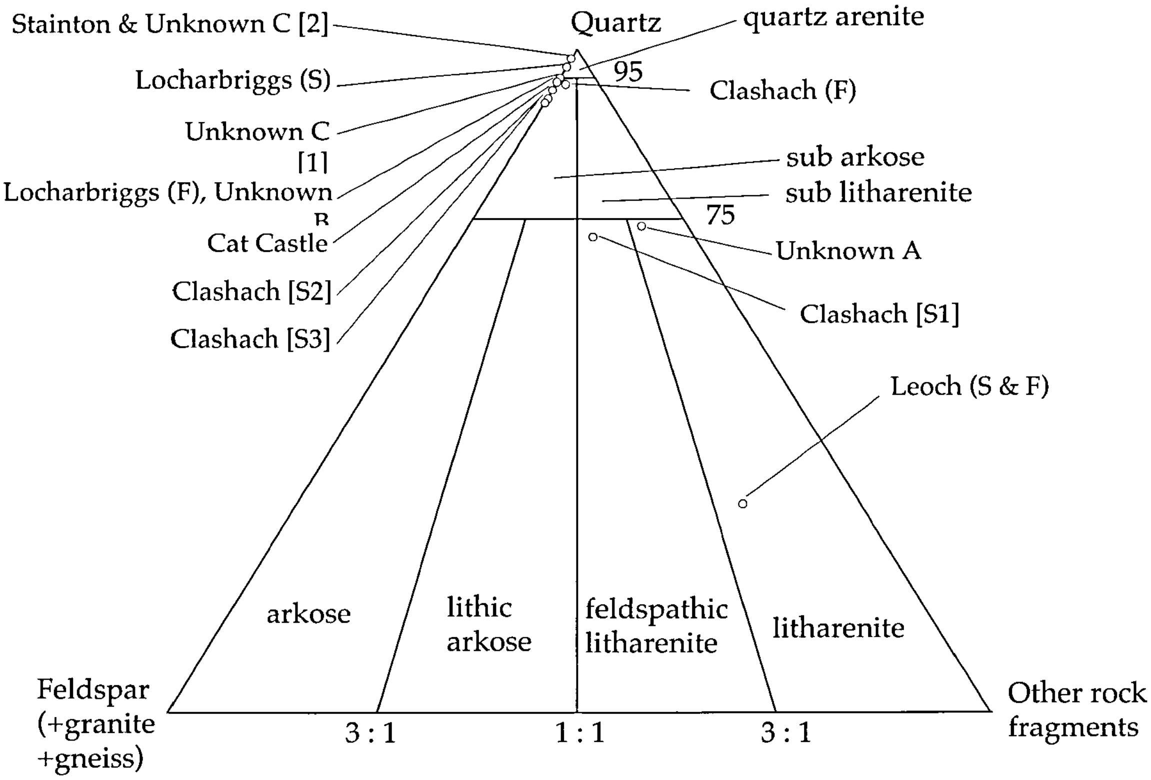


Figure 25 Ternary diagram used for determining the composition of sandstones.
S: soiled, F: fresh, (1): type 1, etc.
(From: Adams, A.E., MacKenzie, W.S. and Guilford, C., .1984, Atlas of Sedimentary Rocks Under the Microscope. Longman)

4.4 Physical property test results

4.4.1 Colour changes to sandstone

4.4.1.1 Colour changes on dry sandstone

Colour data for sandstones following application of consolidants and water repellents are shown in Figure 26. These graphs show the mean colour changes for each sandstone and treatment type. Where a test panel contained more than one sample of any sandstone type, the data have been averaged to give a single figure for that sandstone. The colour before consolidant or water repellent treatment is marked with a square, black symbol. Data points further along each line represent the colour at later stages in the weathering of the sandstones. The number of data points varies as some sandstones were colour measured more often than others. However, in each case the last data point represents the sandstone colour 1.5 years after treatment.

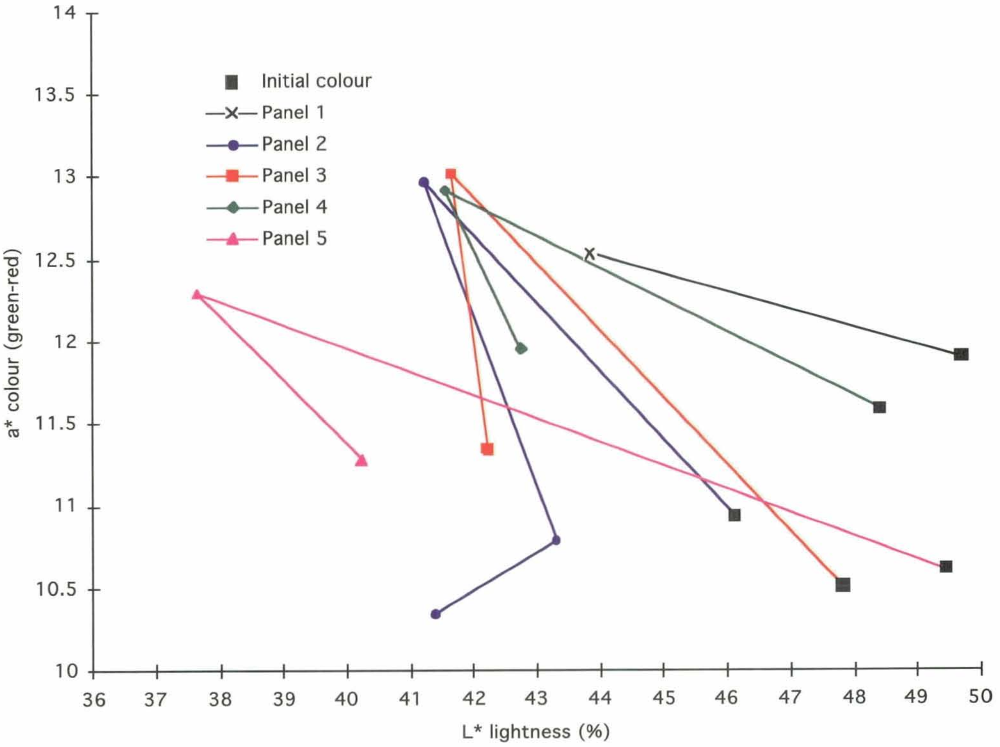


Figure 26a Changes in colour (a) and lightness (L*) of fresh Locharbriggs sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

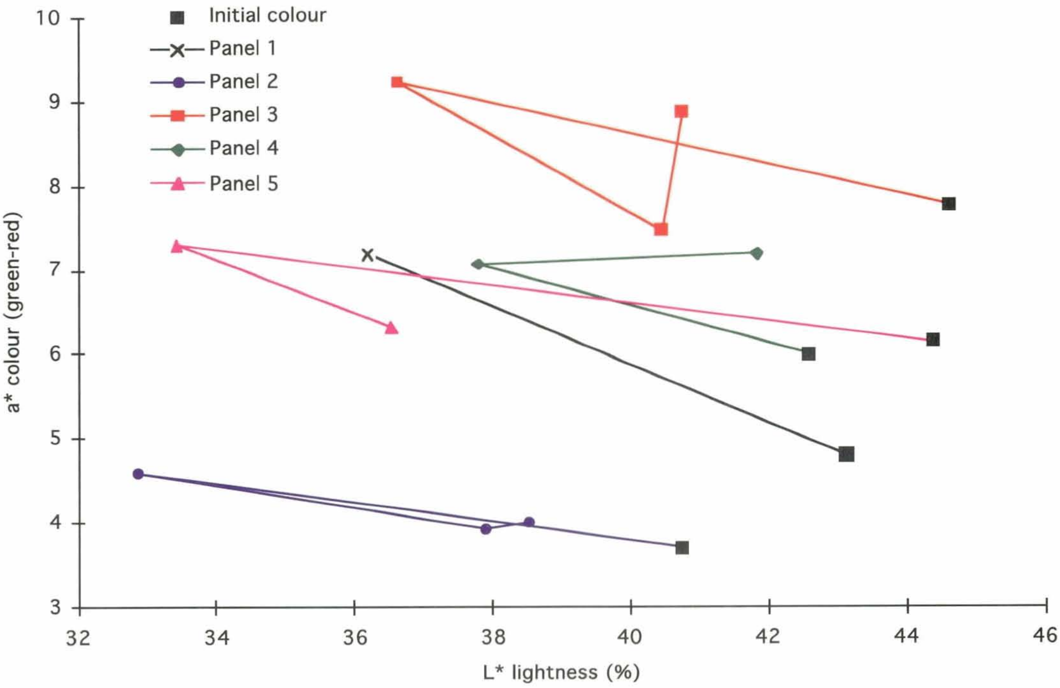


Figure 26b Changes in colour (a) and lightness (L*) of soiled Locharbriggs sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

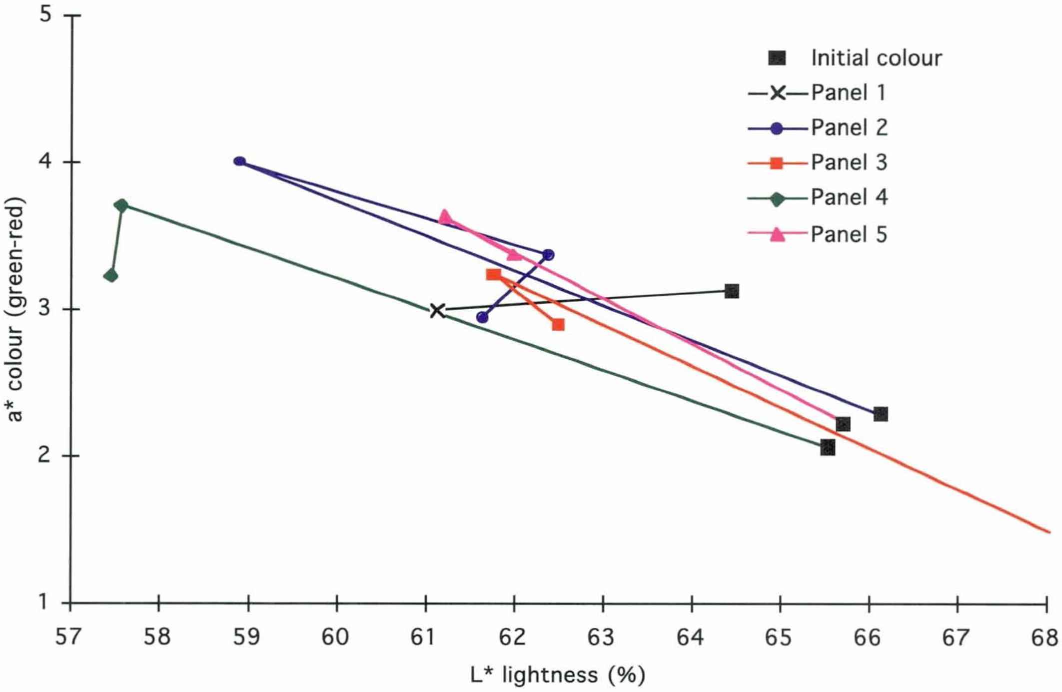


Figure 26c Changes in colour (a) and lightness (L*) of fresh Clashach sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

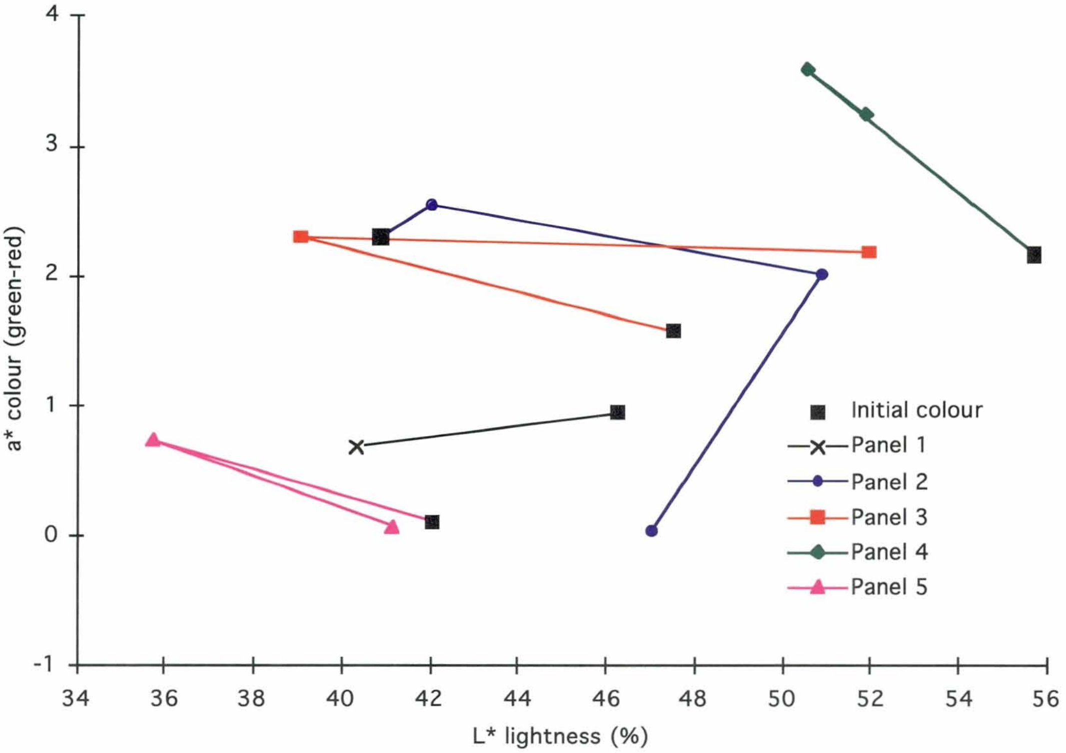


Figure 26d Changes in colour (a) and lightness (L*) of soiled Clashach sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

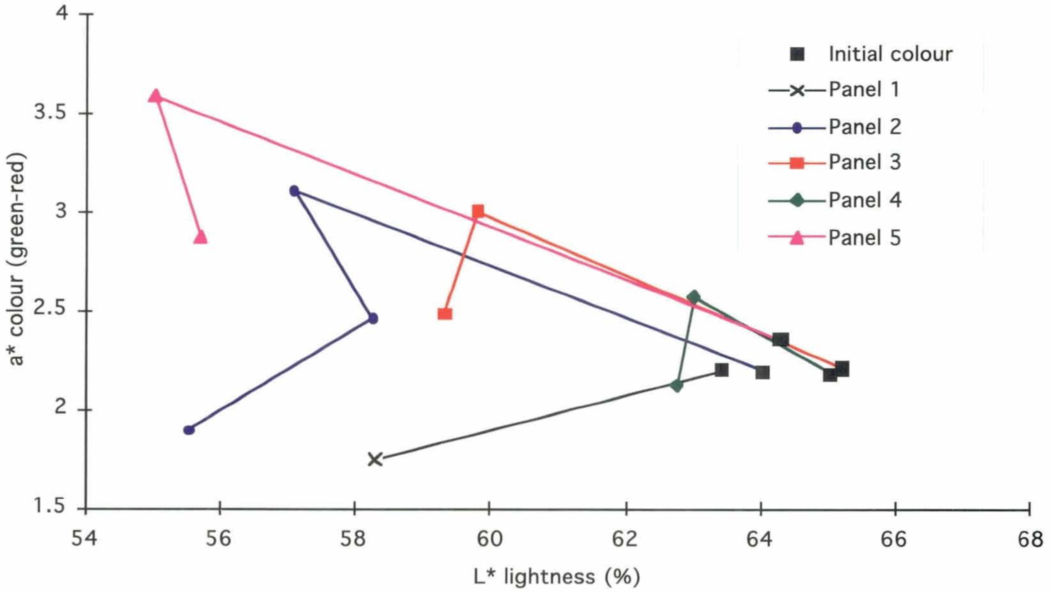


Figure 26e *Changes in colour (a*) and lightness (L*) of fresh Stainton sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

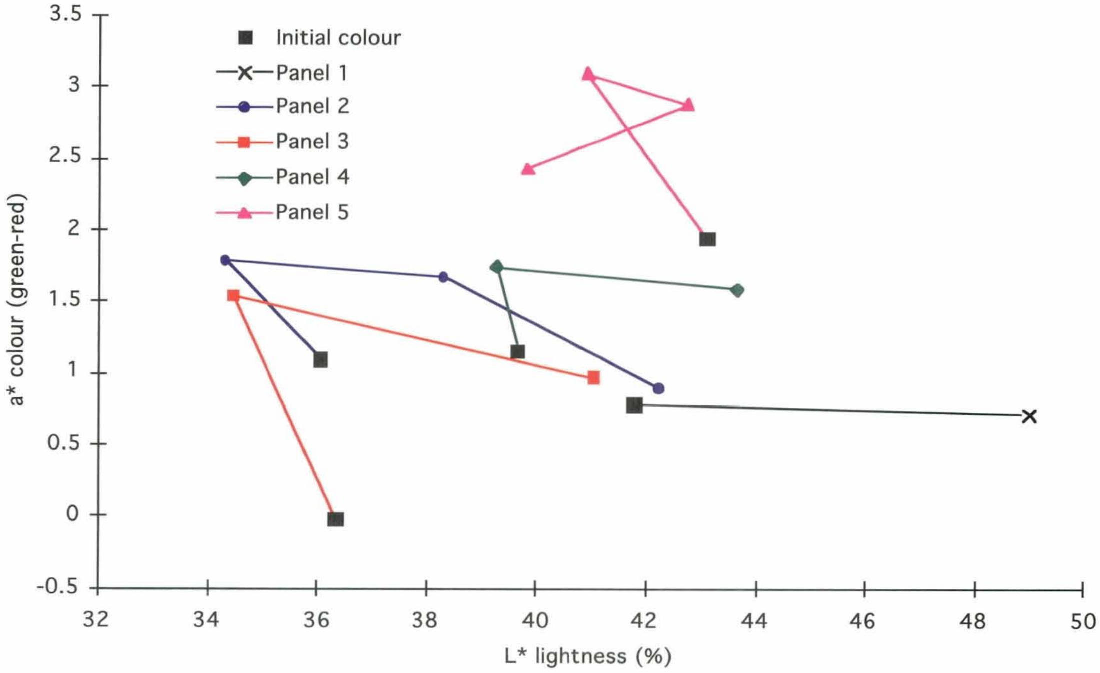


Figure 26f *Changes in colour (a*) and lightness (L*) of soiled Unknown B sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

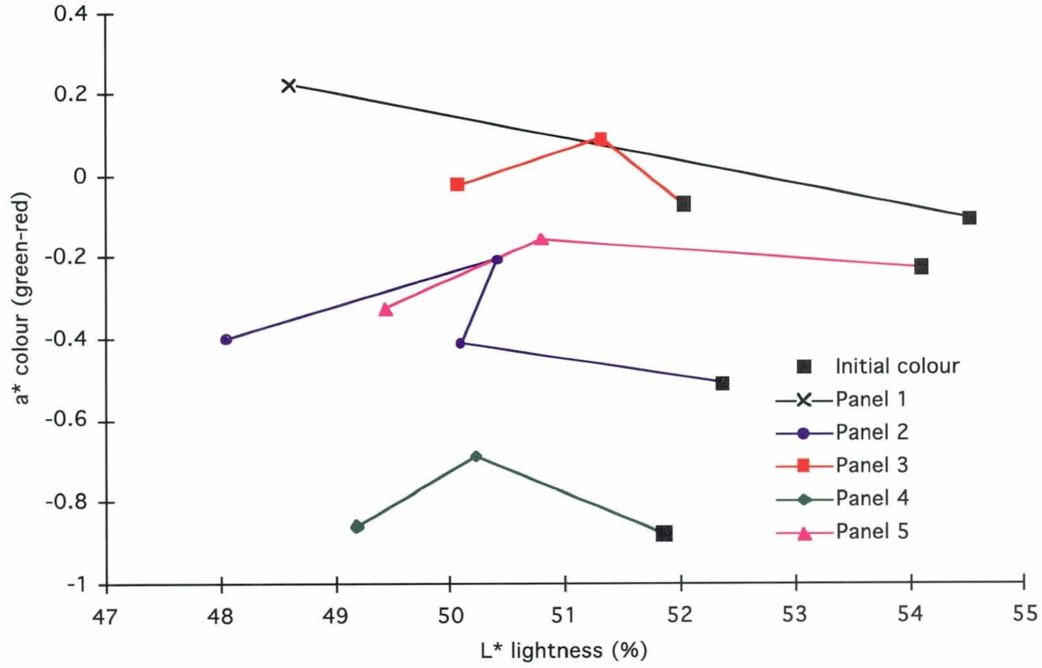


Figure 26g Changes in colour (a) and lightness (L*) of fresh Leoch sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

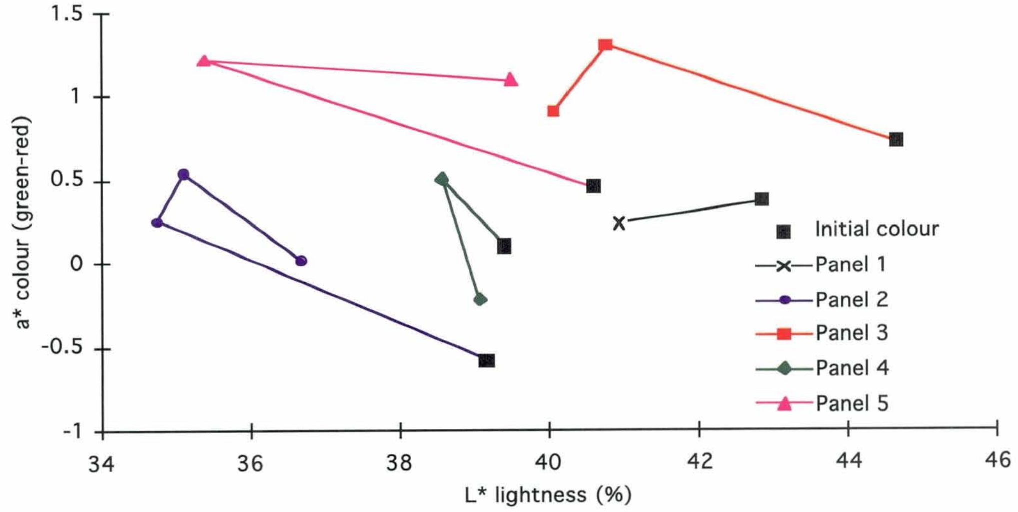


Figure 26h Changes in colour (a) and lightness (L*) of soiled Leoch sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

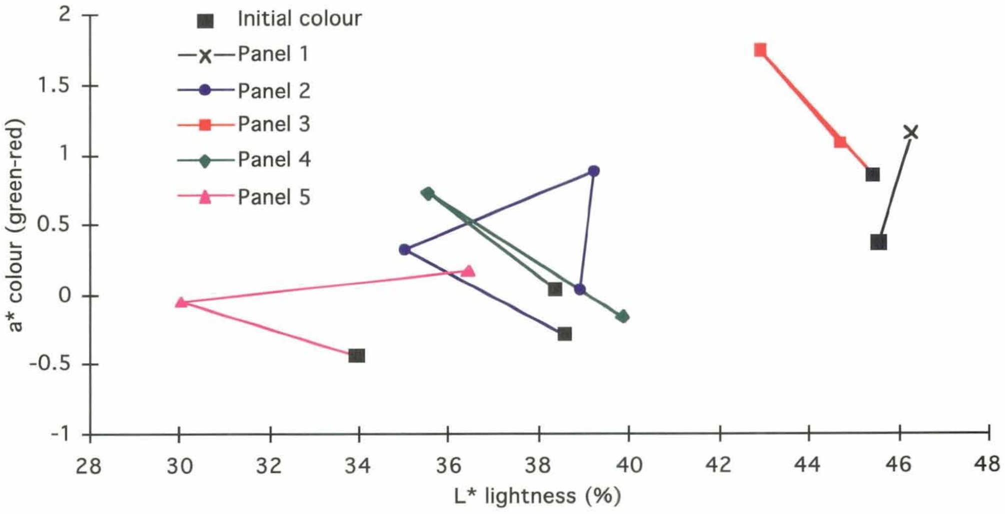


Figure 26i *Changes in colour (a*) and lightness (L*) of soiled Cat Castle sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

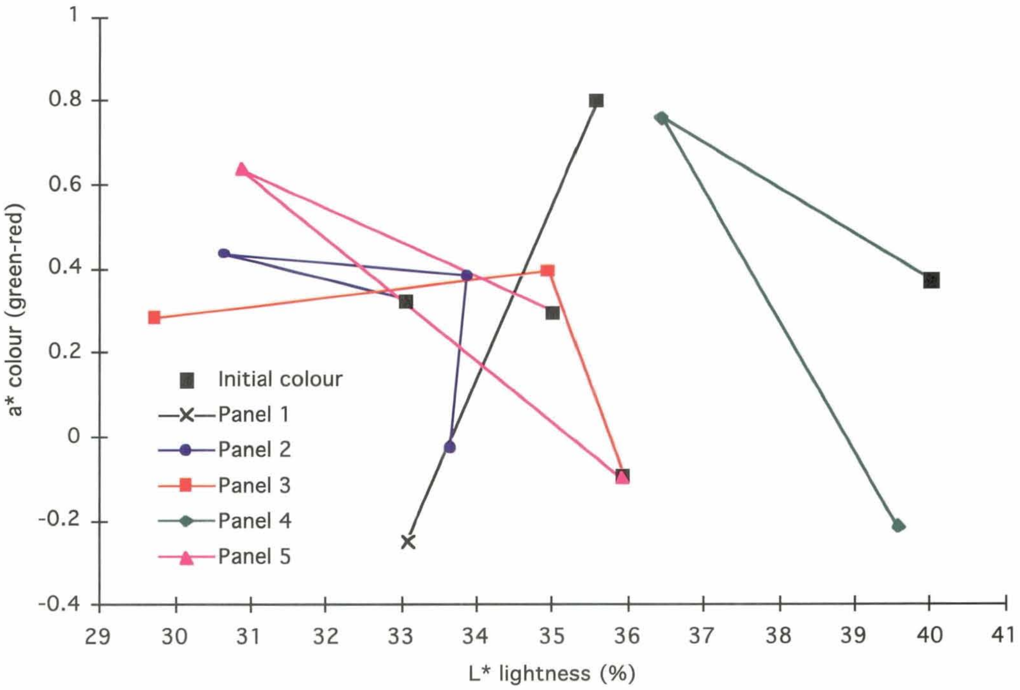


Figure 26j *Changes in colour (a*) and lightness (L*) of soiled Unknown A sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

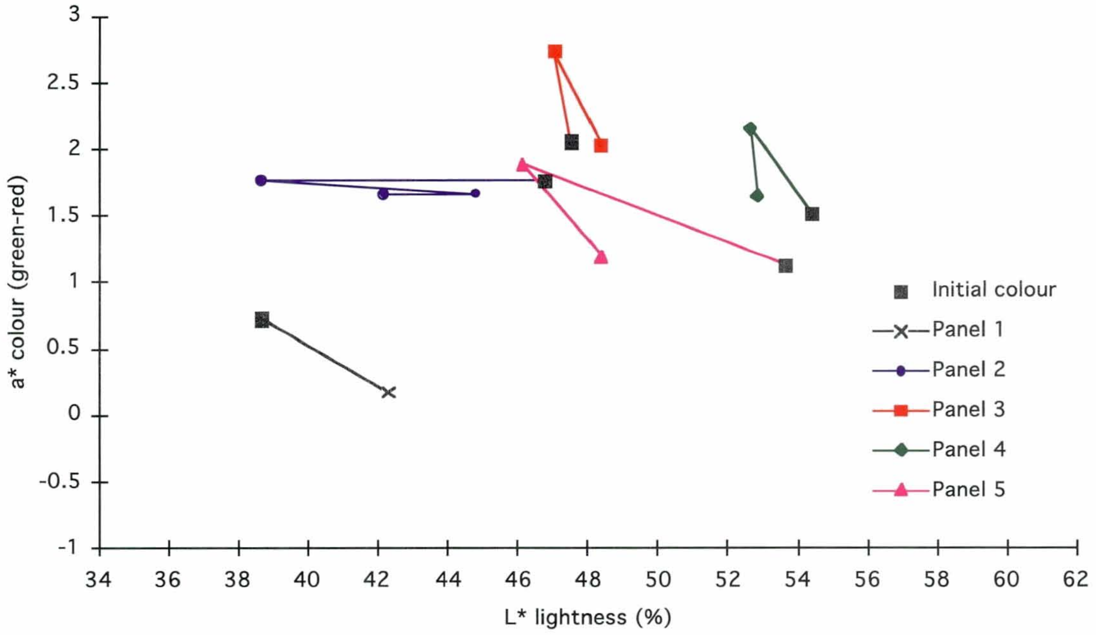


Figure 26k Changes in colour (a) and lightness (L*) of soiled Unknown C sandstones from before treatment (black square) until 1.5 years after treatment. Panel 1: untreated, Panel 2: Consolidant A, Panel 3: Water Rep./Con. C, Panel 4: Water Repellent D, Panel 5: Consolidant B.*

The consolidant and water repellent treatments caused a variety of colour changes on the sandstones. Two months after treatment (2nd data point shown on the graphs) most treated sandstones were darker, redder and more yellow than before treatment. These colour changes were visible to the naked eye. When the colour of the test panels was re-measured after weathering for 1.5 years, the previously measured colour changes had been reduced. That is, the colour of the sandstones was closer to that of the stone before treatment. However, apart from Cat Castle which came close, in no case did the colour of treated sandstone return to its value prior to cleaning. All treated sandstones retained some colour changes 1.5 years after treatment.

To illustrate the changes in colour which occurred between initial treatment and 1.5 years following treatment, Table 6 shows the change in colour (from before treatment) for each treatment type at 2 months and at 1.5 years after treatment. The data are averages for all sandstone types for each treatment and include both initially fresh and soiled sandstones.

Table 6 shows that the colour changes measured after 2 months had all been reduced in value after 1.5 years. Although colour changes caused by application of consolidants and water repellents are reduced over time it is unlikely that the colour of the sandstone would ever return to that of untreated sandstone. However, the colour of untreated sandstone has not remained unchanged itself (Table 6, untreated data). Over 1.5 years of weathering most sandstones show measurable degrees of soiling. This can involve darkening of the surface due to accumulation of soot and possibly some biological components or increased green coloration due to growth of algae.

Treatment	Mean colour change					
	After 2 months			After 1.5 years		
	L*	a*	b*	L*	a*	b*
Untreated	nd	nd	nd	-2.4	0.1	1.2
Consolidant A	-4.4	0.7	0.9	-1.7	-0.2	0.1
Water Rep./Con. C	-4.1	1.0	1.5	-2.3	0.5	1.0
Water Rep. D	-3.4	0.8	1.1	-1.9	0.3	2.3
Consolidant B	-6.3	0.9	1.3	-3.9	0.3	0.9

nd: not determined

Table 6 Mean colour changes (all sandstones), relative to the colour before treatment, for each treatment type. L: lightness (%), a*: +ve red, -ve green, b*: +ve blue, -ve yellow.*

One and a half years after treatment, algal growth was noted on some sandstones. Stones where algal growth was noted were on the control panel or the panel treated with Consolidant A. Algal growth was found on Locharbriggs soiled, "Unknown A" and "Unknown B" on the control panel and on Cat Castle soiled and Clashach soiled on the Consolidant A panel. The greening effects of algal growth can be seen in the colour data for soiled Clashach and "Unknown A" sandstones (Figures 26d and 26j, resp.). On other sandstones the colour changes were too small to be visible.

The mean colour changes shown in Table 6 were averaged for all sandstones types and for soiled and fresh stone. This obscures the fact that colour changes may be larger on some sandstone types than others and changes in degree of soiling also have an effect on coloration. Looking at data from individual sandstones after 1.5 years of weathering (Table 7) we can see that sandstones differed in the degree of colour change caused by treatments. Some stone types underwent relatively large colour changes, for other stone types the degree of colour change was much lower. Table 7 shows colour changes measured on initially ***fresh*** sandstones. Soiled sandstones were excluded because differences in the degree of soiling or in soiling loss during or after treatment could strongly influence the degree of colour change.

At the end of 1.5 years, the measured colour changes caused by treatment were generally not substantially different to those caused by weathering and soiling although visually their appearance may differ from that of untreated sandstones. Treatment with Consolidant B caused the largest colour changes with losses of lightness of up to almost 10% (on Locharbriggs sandstone). Treatment with Water Repellent D caused relatively small colour changes although its effects varied between sandstone types. Sandstones varied in their vulnerability to colour changes. Clashach sandstone (normally a very pale yellow stone) was particularly vulnerable to increased yellow coloration following treatment (shown as an increase in b* colour). This is presumably due to some interaction between the treatments and the iron oxides and hydroxides which give Clashach sandstone its colour. Some treatments also caused pronounced darkening of both Clashach and Locharbriggs sandstones. Leoch sandstone generally had the smallest colour changes on treatment. Leoch sandstone has a low porosity and permeability and took up relatively little consolidant or water repellent on treatment (Section 4.2.1). Presumably the relatively small amount of consolidant or water repellent in this sandstone was responsible for the relatively small colour change on treatment. In fact, some treated samples of fresh Leoch sandstone showed quite a marked reduction in soiling rate (as measured by L*) compared to untreated sandstone.

Sandstone	**Mean colour change by**		**Consolidant A**	**Mean colour change on untreated stone**			**Sandstone**
	L*	**a***	**b***	**L***	**a***	**b***	
Locharbriggs	-4.7	-0.6	-2.5	-5.9	0.6	0.6	**Locharbriggs**
Clashach	-4.5	0.7	3.6	-3.3	-0.1	1.3	**Clashach**
Stainton	-8.5	-0.3	0.5	-5.1	-0.5	2.3	**Stainton**
Leoch	-4.3	0.1	0.4	-5.9	0.3	0.9	**Leoch**

	Mean colour change by Consolidant B		
Sandstone	L*	a*	b*
Locharbriggs	-9.2	0.7	-0.2
Clashach	-5.6	1.2	4.2
Stainton	-8.6	0.5	0.6
Leoch	-4.7	-0.1	1.8

	Mean colour change by Water Rep./Con. C		
Sandstone	L*	a*	b*
Locharbriggs	-5.6	0.8	2.0
Clashach	-5.2	1.2	4.0
Stainton	-5.9	0.3	2.7
Leoch	-2.0	0.0	0.7

	Mean colour change by Water Repellent D		
Sandstone	L*	a*	b*
Locharbriggs	-5.7	0.4	2.4
Clashach	-8.1	1.2	5.5
Stainton	-2.3	-0.1	2.1
Leoch	-2.7	0.0	0.1

On average, after 1.5 years of weathering, the degree of colour change on ***fresh*** sandstones caused by each treatment was:

	Mean colour change		
Treatment	**L***	**a***	**b***
Water Repellent D	-4.7	0.4	2.5
Water Rep./Con. C	-4.7	0.6	2.3
None	-5.1	0.1	1.3
Consolidant A	-5.5	0.0	0.5
Consolidant B	-7.0	0.6	1.6

*Table 7 Colour changes after 1.5 years weathering for initially **fresh** sandstone types. The colour changes on untreated sandstone (box on right) are due to weathering and soiling alone.*

These data are ranked in order of lightness changes. While sandstones treated with Consolidant A and Consolidant B were darker than would be expected from weathering and soiling (treatment "None" above), the other two treatments (Water Rep./Con. C and Water Repellent D) appeared to have reduced the rate of lightness loss caused by soiling accumulation. Consolidant A and Consolidant B have minimal water repellency while Water Rep./Con. C and Water Repellent D are water repellent. Therefore, although all treatments initially caused darkening (Figure 26), in the longer term the water repellent treatments appear to have reduced the rate of darkening of the fresh sandstones by soiling accumulation. On stones treated with non-water repellent consolidants the lightness change after 1.5 years is a combination of changes caused by the treatment and by soiling accumulation. Colour changes other than darkening were also measured (a* & b*). On fresh sandstones all treatments except Consolidant A caused colour changes (reddening and yellowing) which were larger than those caused by weathering.

On sandstone blocks that were initially soiled, consolidant or water repellent treatment (which involves brushing the surface with solvents) and later washing and brushing to remove debris from coring could remove soiling from the stone surface. This results in a stone which may appear brighter after treatment despite the fact that consolidant and water repellent treatments have been shown to cause darkening of surfaces. This effect has been observed on initially soiled Cat Castle, Clashach, Unknown A, Unknown B and Unknown C sandstones (Figure 26). No consistent results can be derived from measuring soiling changes since the degree of soiling loss from the sandstones will depend on the soiling type (e.g. biological or particulate), the degree of attachment to the stone and the re-soiling rate of the stone. However, despite the difficulty in interpreting colour changes on soiled sandstone, consolidant and water repellent treatments on soiled sandstones can cause colour changes similar to those observed on unsoiled stone.

4.4.1.2 Colour changes on wet sandstone

When the consolidant and water repellent treatments on the test panels had matured for 1.5 years the colour of the sandstones was compared when wet and dry. The aim of this experiment was to determine whether the colour changes caused by treatment were more or less visible when the sandstone was wet or dry. The sandstone blocks were wetted a few minutes before colour measurement by spraying with water for about 1 minute per square meter.

The predominant changes measured on wetting were darkening of the surface although colour changes also occurred (Figure 27). For most sandstone types, the degree of lightness change was greater on the untreated sandstone than on water repellent or consolidant treated sandstones. This occurred because water was more easily absorbed into the untreated sandstone and therefore caused the greatest colour change. On sandstones where water absorption was prevented or reduced, the degree of lightness change was less.

The more water repellent the treatment, the less the degree of colour change on wetting. Sandstones treated with Water Repellent D showed relatively little colour change on wetting and untreated sandstones the most. The changes in lightness are summarised in Figure 28. From the data in Figure 28 it can be observed that the order of treatments in terms of degree of colour change on wetting was:

Least colour change on wetting		Water Repellent D
	↓	Water Rep./Con. C
		Consolidant B
		Consolidant A
Most colour change on wetting		Untreated

The lightness and colour changes caused by wetting of untreated sandstones were similar to those caused by consolidant and water repellent treatment. This means that these treatments have a similar effect on the sandstones appearance as wetting. However, consolidant and water repellent treatments differed in the degree of colour change they caused. Table 8 shows the lightness and colour changes caused by wetting compared with those caused by consolidant and water repellent treatments on fresh sandstones (where there were no complicating effects of changes in soiling level). It can be observed that the lightness and colour changes were similar for both wetting and consolidant or water repellent treatment although effects varied and wetting caused the greatest degree of darkening.

	Wetting	**Con. A**	**Con. B**	**Water Rep./Con. C**	**Water Rep. D**
L (lightness)*					
Locharbriggs	-12.2	-4.7	-9.2	-5.6	-5.7
Clashach	-11.9	-4.5	-5.6	-5.2	-8.1
Stainton	-13.8	-8.5	-8.6	-5.9	-2.3
Leoch	-16.2	-4.3	-4.7	-2.0	-2.7
L* mean	**-13.5**	**-5.5**	**-7.0**	**-4.7**	**-4.7**
a (green-red)*					
Locharbriggs	0.3	-0.6	0.7	0.8	0.4
Clashach	1.7	0.7	1.2	1.2	1.2
Stainton	0.0	-0.3	0.5	0.3	-0.1
Leoch	0.9	0.1	-0.1	0.0	0.0
a* mean	**0.7**	**0.0**	**0.6**	**0.6**	**0.4**
b (blue-yellow)*					
Locharbriggs	-0.8	-2.5	-0.2	2.0	2.4
Clashach	3.7	3.6	4.2	4.0	5.5
Stainton	2.9	0.5	0.6	2.7	2.1
Leoch	-1.2	0.4	1.8	0.7	0.1
b* mean	**1.2**	**0.5**	**1.6**	**2.3**	**2.5**

Table 8 Lightness (L) and colour (a* & b*) changes caused by wetting compared with those caused by consolidant and water repellent treatments on fresh sandstones (after 1.5 years).*

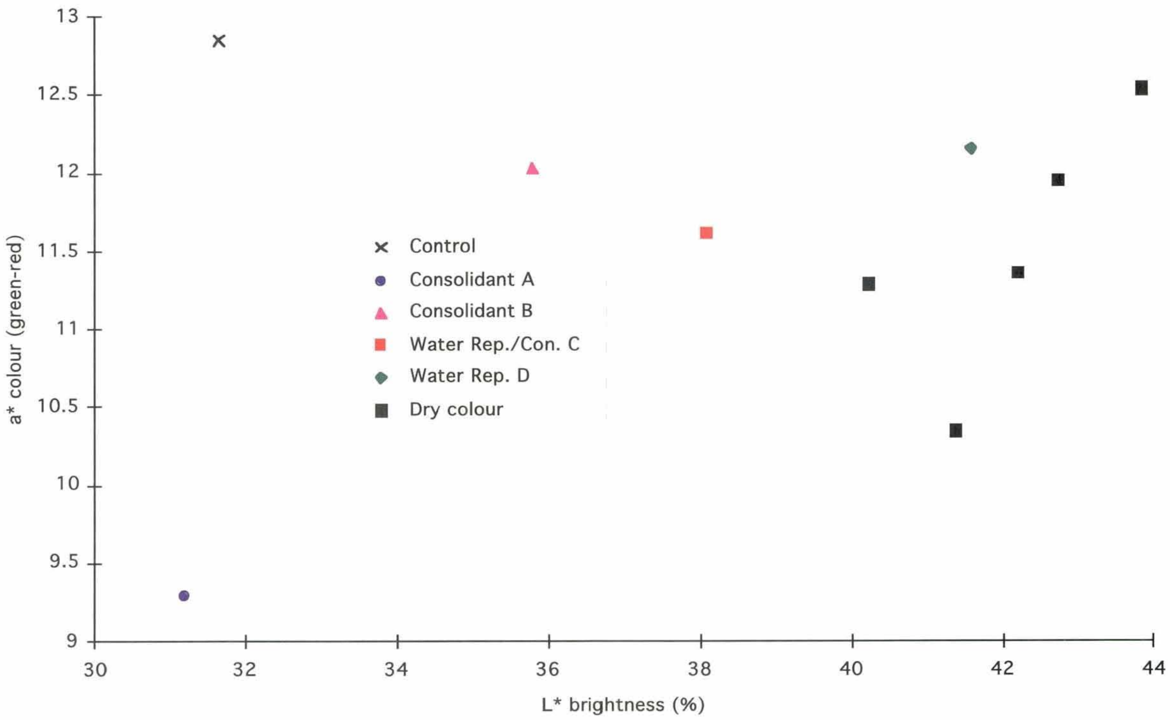


Figure 27a Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated **fresh Locharbriggs** sandstone.*

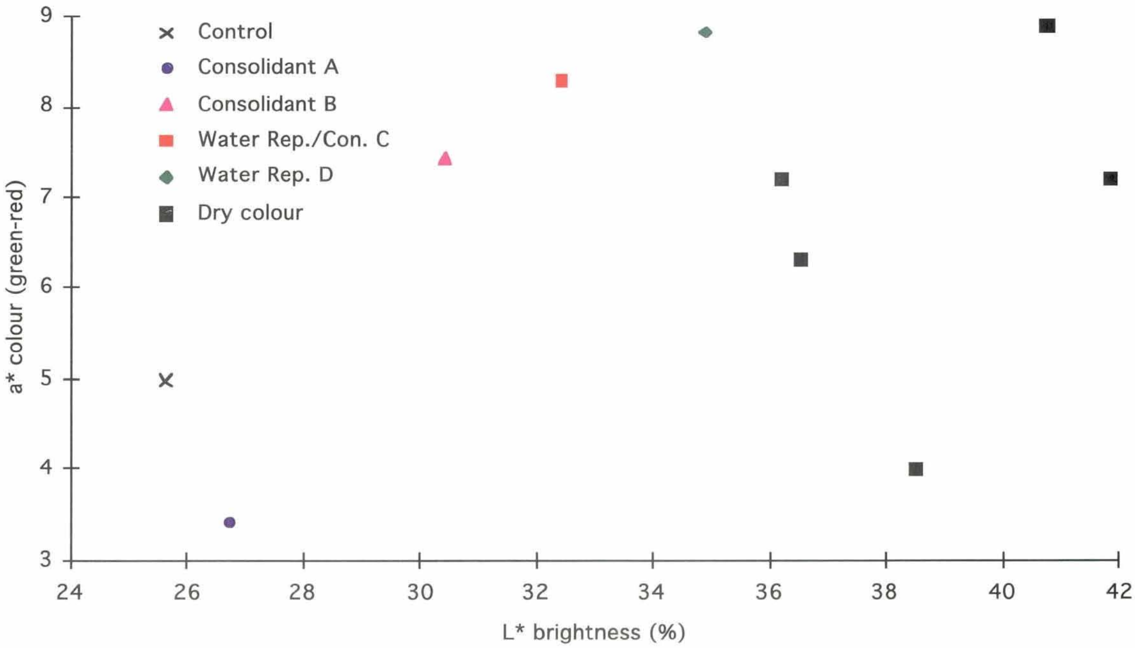


Figure 27b Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated **soiled Locharbriggs** sandstone.*

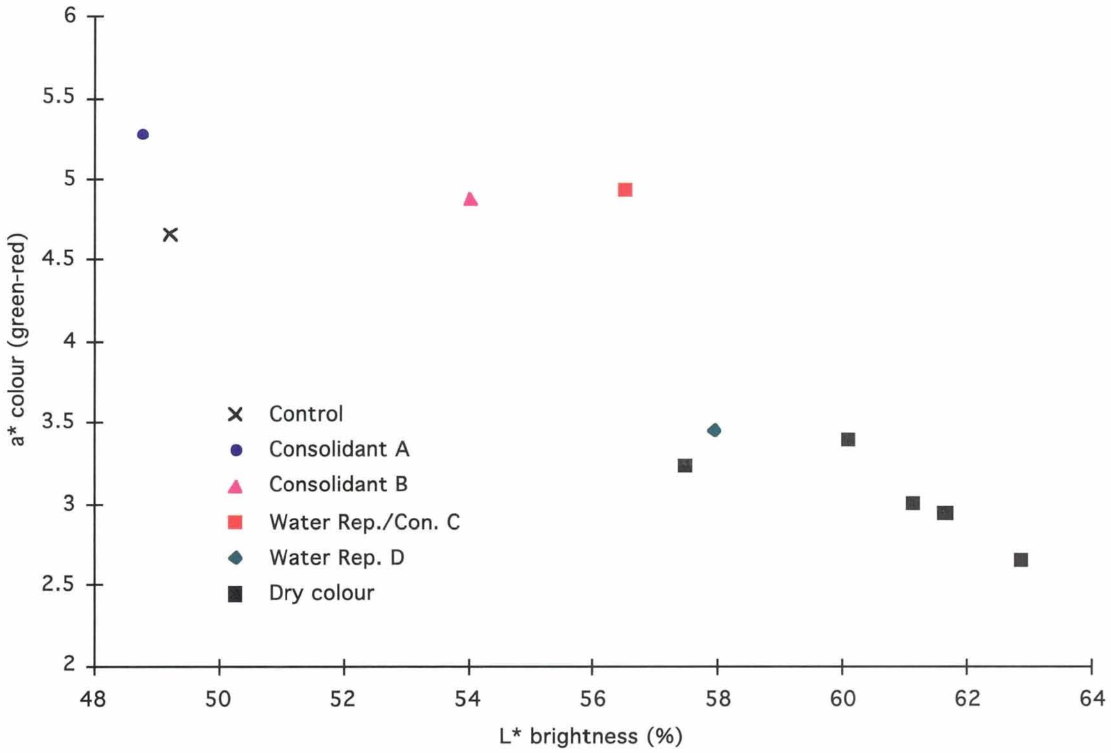


Figure 27c Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***fresh Clashach*** *sandstone.*

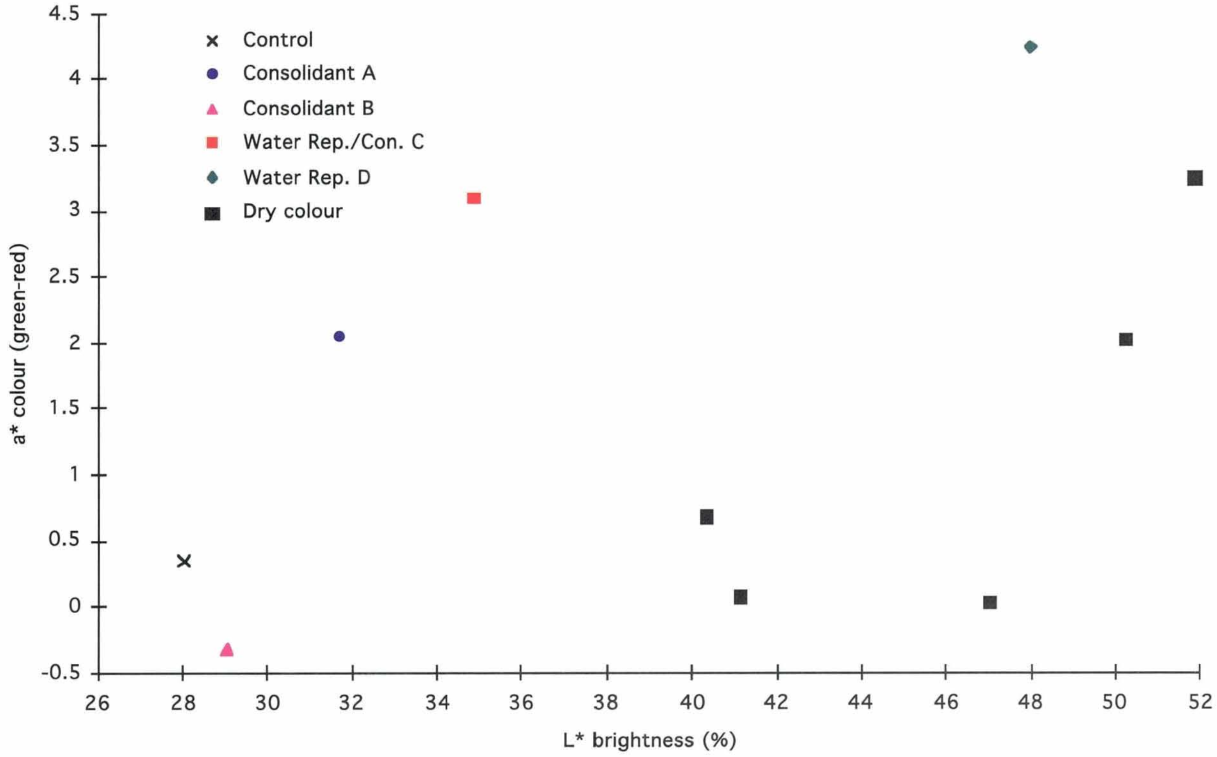


Figure 27d Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***soiled Clashach*** *sandstone.*

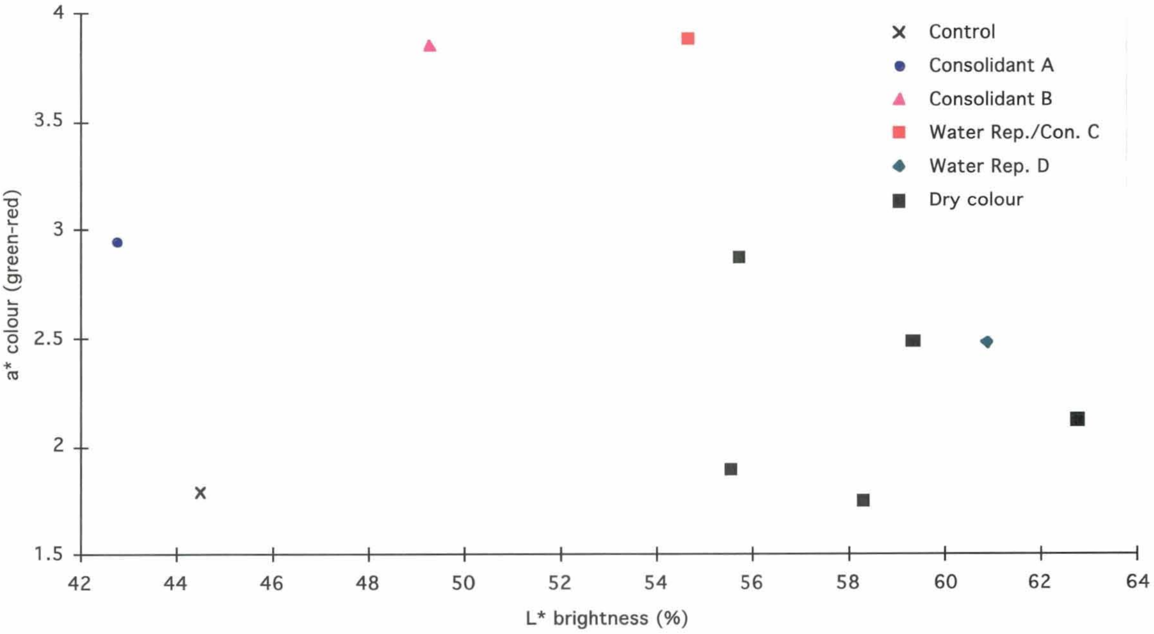


Figure 27e *Showing the difference in colour (a*) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***fresh Stainton*** *sandstone.*

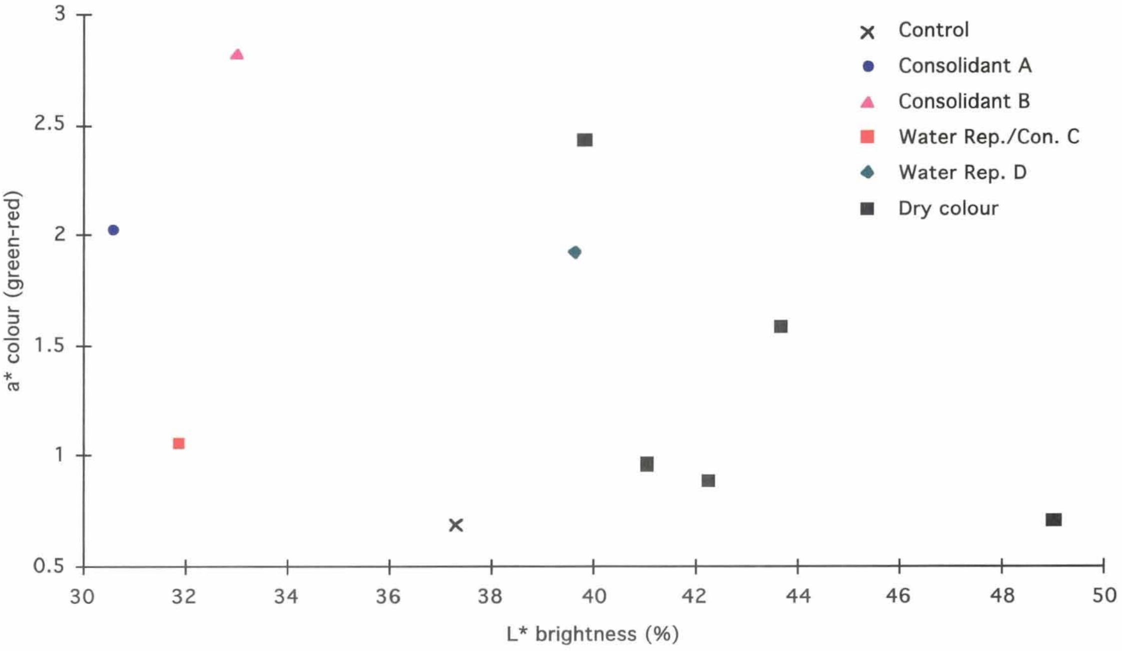


Figure 27f *Showing the difference in colour (a*) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***soiled Unknown B*** *sandstone.*

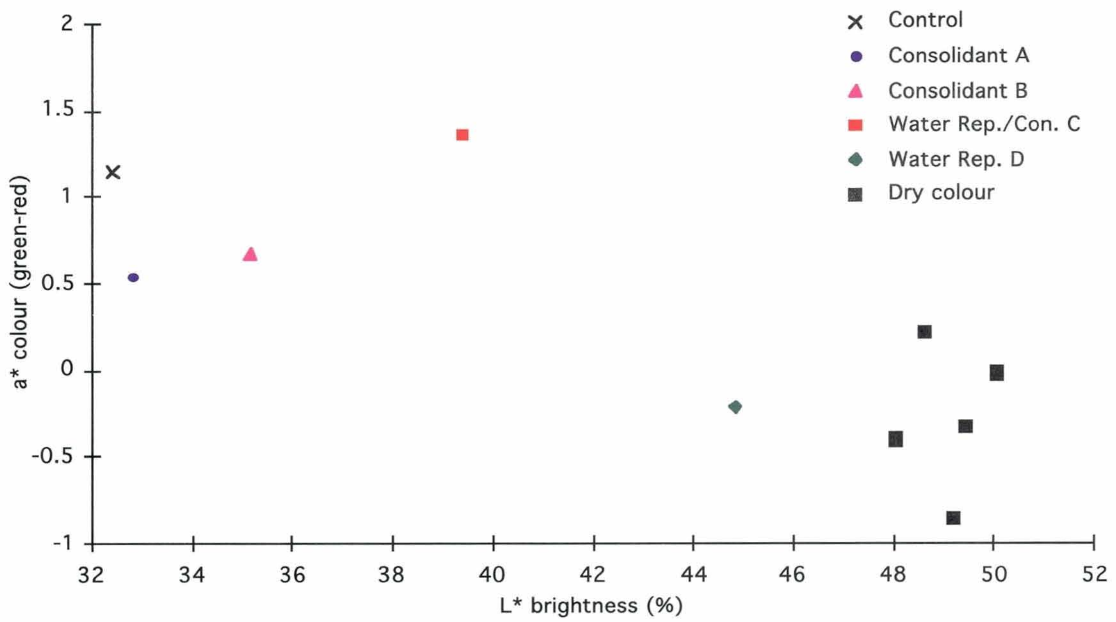


Figure 27g Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***fresh Leoch*** *sandstone.*

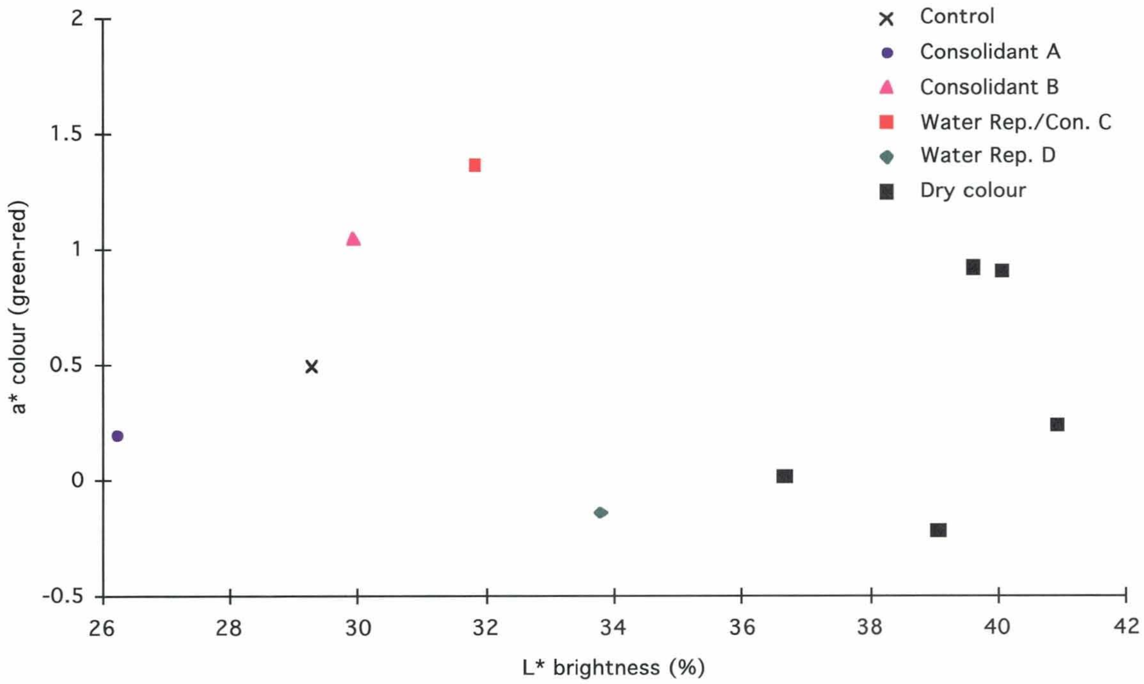


Figure 27h Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***soiled Leoch*** *sandstone.*

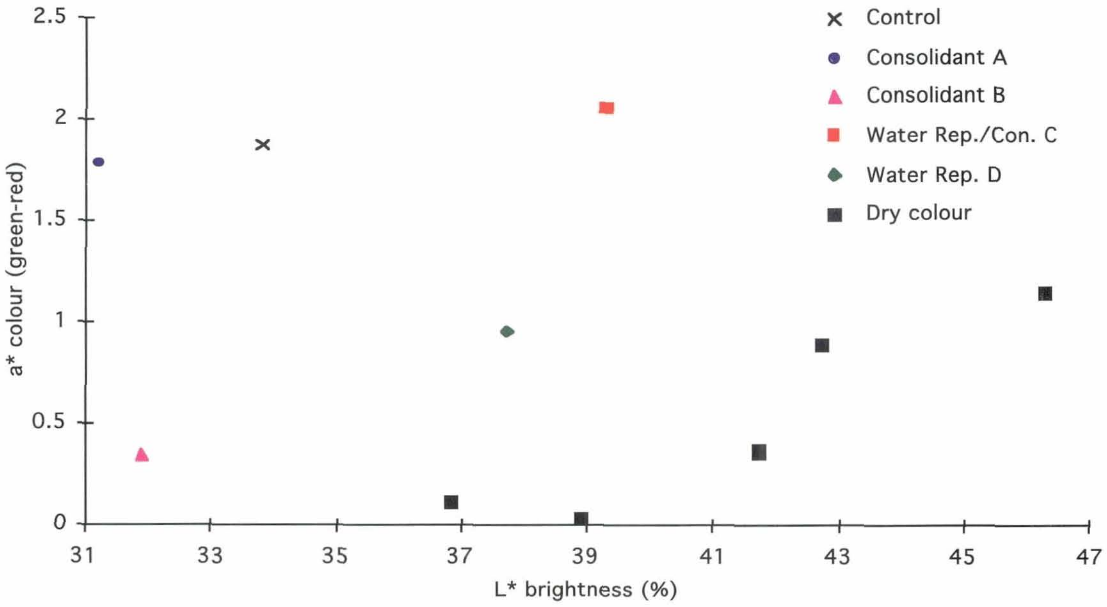


Figure 27i Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***soiled Cat Castle*** *sandstone.*

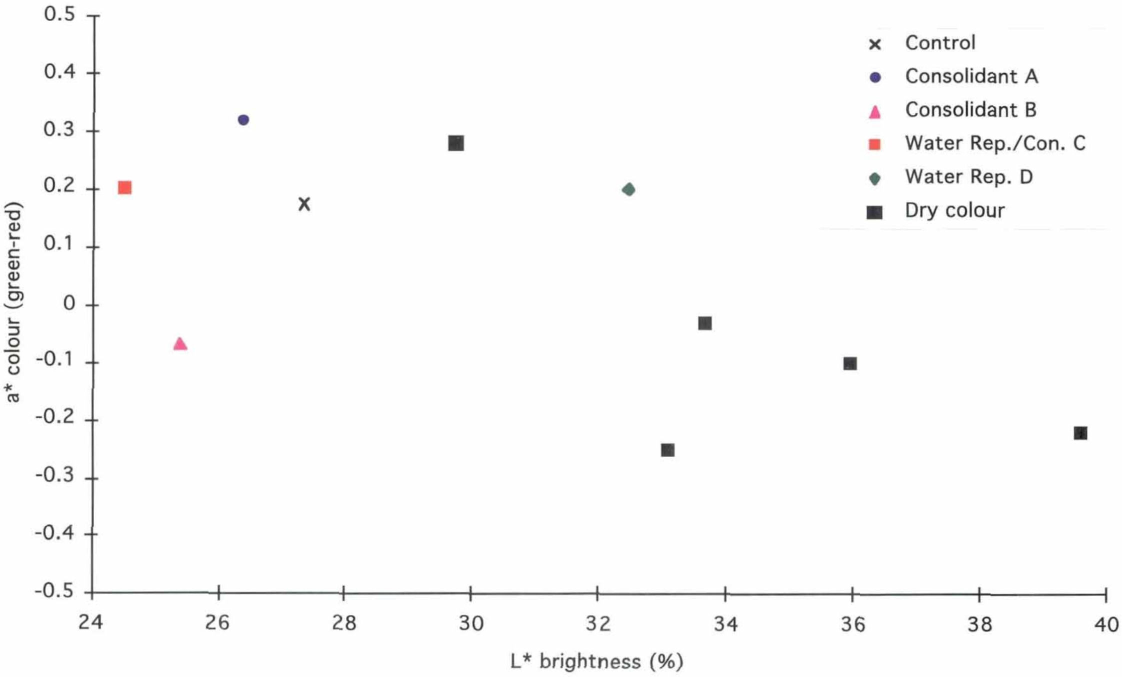


Figure 27j Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***soiled Unknown A*** *sandstone.*

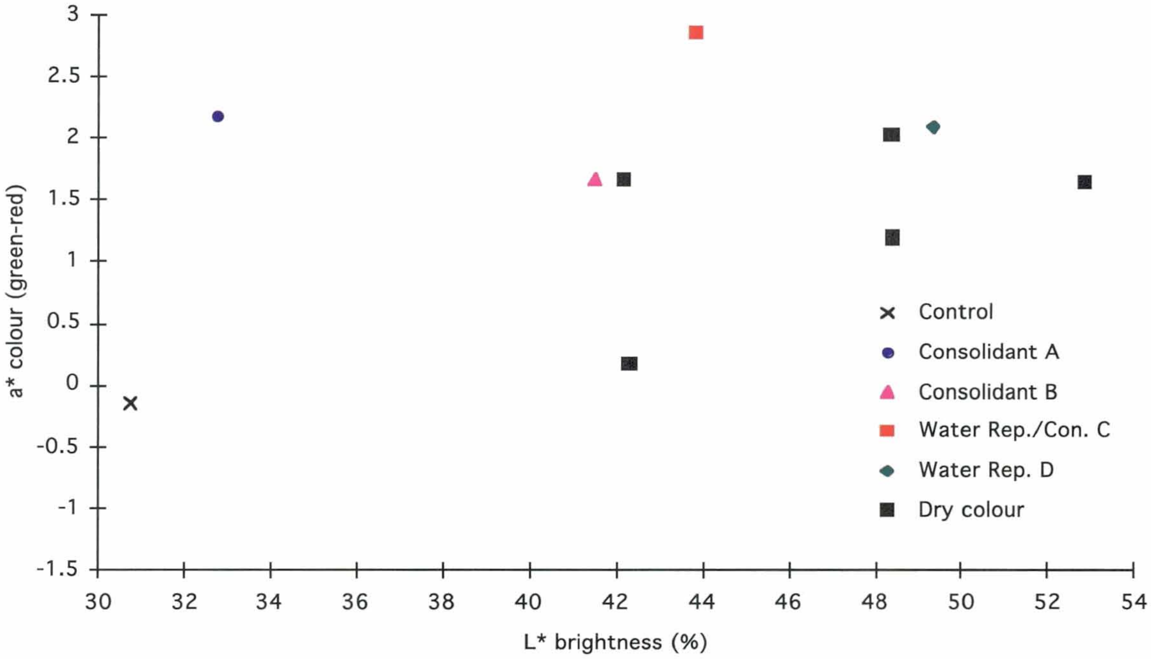


Figure 27k Showing the difference in colour (a) and lightness (L*) between dry (black square) and wet (small symbol) treated and untreated* ***soiled Unknown C*** *sandstone.*

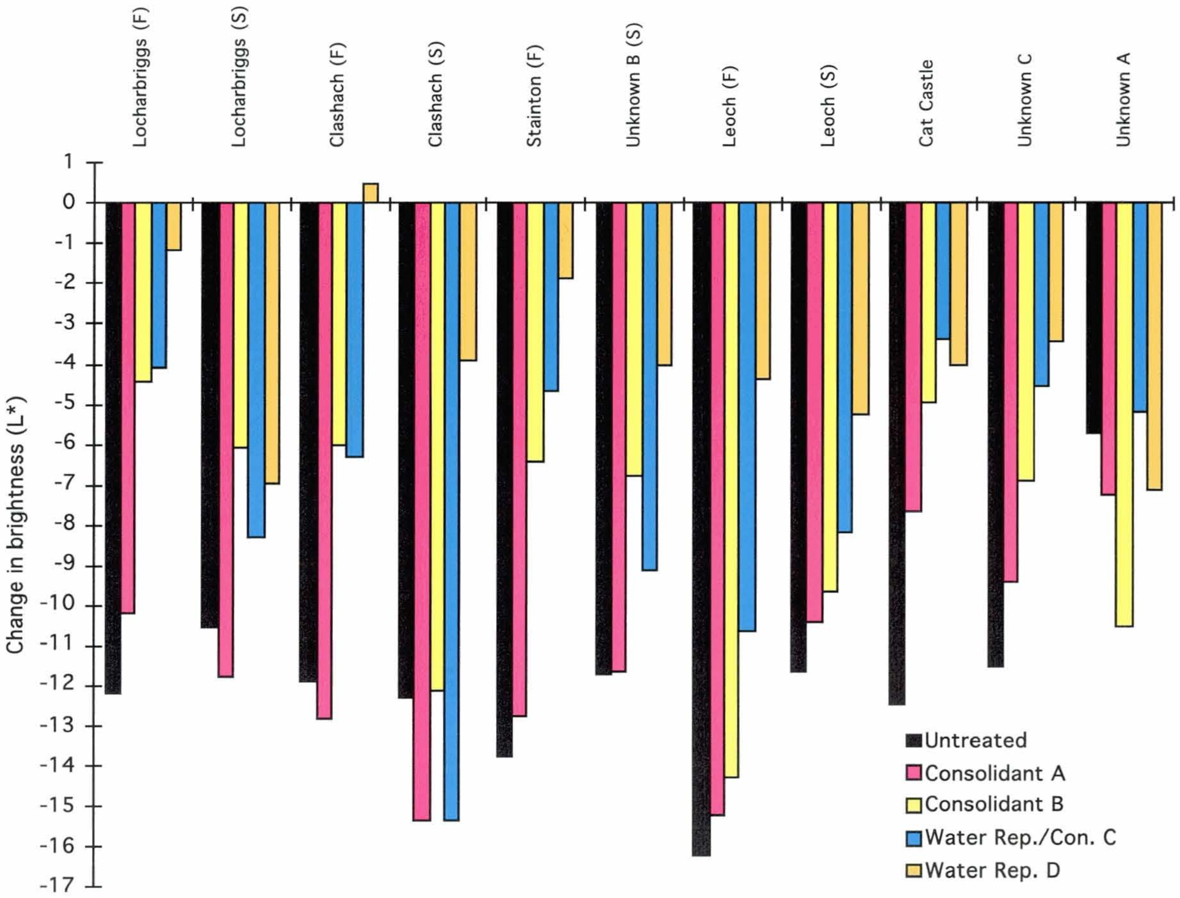


Figure 28 Bar chart showing the change in lightness (ΔL) caused by wetting of treated and untreated sandstones relative to their lightness when dry.*

4.4.2 Water absorption rates of sandstones

The water absorption rates of the sandstone blocks in the test panels at Aberdeen were measured before and after treatment using the methodology given in Section 3.3.3. Water absorption rates were measured before treatment and after maturation of the treatment. The results are shown graphically in Figure 29. No results are given for Leoch sandstone. The permeability of this sandstone was so low that water absorption rates were close to zero and were not measurable by this technique. Since water absorption rates can vary from place to place on a stone, measurements before and after treatment were carried out at the same position on the stone. Although no treatment was applied to Panel 1, two measurements of water absorption were made (leaving time for the stone to dry out between measurements) to see whether any changes caused by the act of measurement alone could affect moisture absorption rates. For instance, it is possible that on previously soiled sandstone some soiling could be removed from the surface during the first measurement and this could increase moisture absorption in the second measurement. Results indicated that there could be both slight increases or decreases in water absorption rate at the second measurement. However, there was no indication that measurement substantially or consistently affected water absorption.

Locharbriggs sandstone

For fresh Locharbriggs sandstone there was a clear difference in water absorption rates before and after treatment with much slower rates of water absorption after treatment (Figure 29a). There was little difference in the two moisture absorption rates measured on Panel 1 (control) indicating that measurement of moisture absorption had little effect on subsequent measurements. While the other treatments had greatly reduced moisture penetration, the panel treated with Consolidant A (Panel 2) had a reduced but still moderate moisture absorption rate after treatment. Consolidant A is a consolidant with minimal water repellent properties. Closer examination of the initial stages of moisture penetration on the Consolidant A treated sandstone showed that moisture absorption rates were initially slow, then speeded up after about 200 seconds (Figure 29e). This was not due to any leakage of water from the measuring device. This pattern of water absorption was different to almost all other moisture absorption measurements where the rate was initially faster and slowed over time (but see "Clashach sandstone" below).

For soiled Locharbriggs sandstone there was a clear difference in water absorption rates before and after treatment with much slower rates of water absorption after treatment (Figure 29b). There was relatively little difference in the moisture absorption rates on the untreated control sample between the two measurements; moisture absorption was slightly faster on the second run perhaps due to slight soiling removal during the first run. One of the blocks (Consolidant B) had a rather slower moisture absorption rate before treatment. After treatment with Consolidant B the sandstone had an initially faster water absorption rate (for the first few seconds) than before treatment which later slowed dramatically.

Clashach sandstone

For fresh Clashach sandstone there was a clear difference in water absorption rates before and after treatment with much slower rates of water absorption after treatment (Figure 29c). Clashach sandstone can vary in its moisture absorption rate between samples and both the Consolidant B sandstone before treatment and the control sample had relatively slow moisture absorption rates. There was little difference in the two moisture absorption rates on control samples indicating that measurement of moisture absorption had little effect on subsequent measurements. As was found with Locharbriggs sandstone, the panel treated with Consolidant A (Panel 2) had a reduced but still moderate moisture absorption rate after treatment while the panels with other treatments had greatly reduced moisture penetration. Again, similarly to that which was observed on the Locharbriggs sandstone, during the initial stages of moisture penetration on the Consolidant A treated sample, moisture absorption rates were initially slow, then speeded up after about 400-800 seconds (Figure 29e), again this was not due to any leakage of water.

On soiled Clashach sandstone (Figure 29d) there was a clear difference in water absorption rates before and after treatment with much slower rates of water absorption after treatment. There was relatively little difference in the water absorption rates between the first and second measurements on the control panel The apparently increasing speed of water absorption measured on Consolidant B before treatment is believed to have been caused by a slow leak from the apparatus. There was no evidence of initially faster water absorption after treatment as was noted on some other sandstones.

Stainton sandstone

Untreated samples of Stainton sandstone did not vary greatly in their water absorption rates (Figure 29f). There was a clear difference in water absorption rates before and after treatment with overall much slower rates of water absorption after treatment. However, on many treated samples the initial water absorption rates (in the first few seconds) were faster after treatment, slowing dramatically later (Figure 29g). This effect was noticed with the treatment Water Repellent D and on one sandstone treated with Consolidant B (although not on the second sandstone with the same treatment). On the sandstones treated with Consolidant A initial water absorption rates were unchanged from those observed before treatment. There was no evidence of the speeding up of water absorption noticed on Locharbriggs and Clashach sandstone. On Water Rep./Con. C treated sandstones the water absorption rates were significantly slower after treatment.

"Unknown A" sandstone (soiled)

On this heavily soiled sandstone, some samples showed greater water absorption (i.e. faster absorption and a greater amount of water taken up) after treatment than before (Figure 29h). The two runs on the control sandstone showed little difference in water absorption rates. Treatments which gave greater water absorption after application were Consolidant A, Consolidant B and Water Rep./Con. C. On the panel treated with Water Repellent D the stone initially took up water more rapidly then slowed.

"Unknown B" sandstone (soiled)

Due to the large number of Unknown B sandstone samples the data has been split into two graphs (Figures 29i & j). On the two sandstone samples on Panel 1 (control), one had faster water absorption on the first run and the other was faster on the second run. On some treated samples, initially faster water absorption was noted before the rate slowed dramatically. This effect was most noticeable on the two samples treated with Consolidant B but was also noted on one Consolidant A treated sample, one Water Repellent D treated sample and on both Water Rep./Con. C treated samples.

Cat Castle sandstone (soiled)

Due to the large number of Cat Castle sandstone samples the data has been split into two graphs (Figures 29k & l). Measurements of water absorption rates on the control panel showed little difference between measurements; for one sandstone block rates were virtually identical, on the other the second measurement gave a rate which was slightly slower than the first. On almost all samples the water absorption rates were slower after treatment although effects varied from relatively slight to substantially slower. Only one sandstone treated with Water Rep./Con. C showed initially faster water absorption after treatment as has been observed on some other samples.

"Unknown C" sandstone (soiled)

There was a clear difference in water absorption rates before and after treatment with much slower rates overall on the treated samples (Figure 29m). There was little difference in the rates measured in the two runs on the untreated sample. Again, some treated samples showed initially faster water absorption before the rate slowed dramatically. This effect was noted on the Consolidant B treated sample and the Water Rep./Con. C treated sample but not with Consolidant A or Water Repellent D.

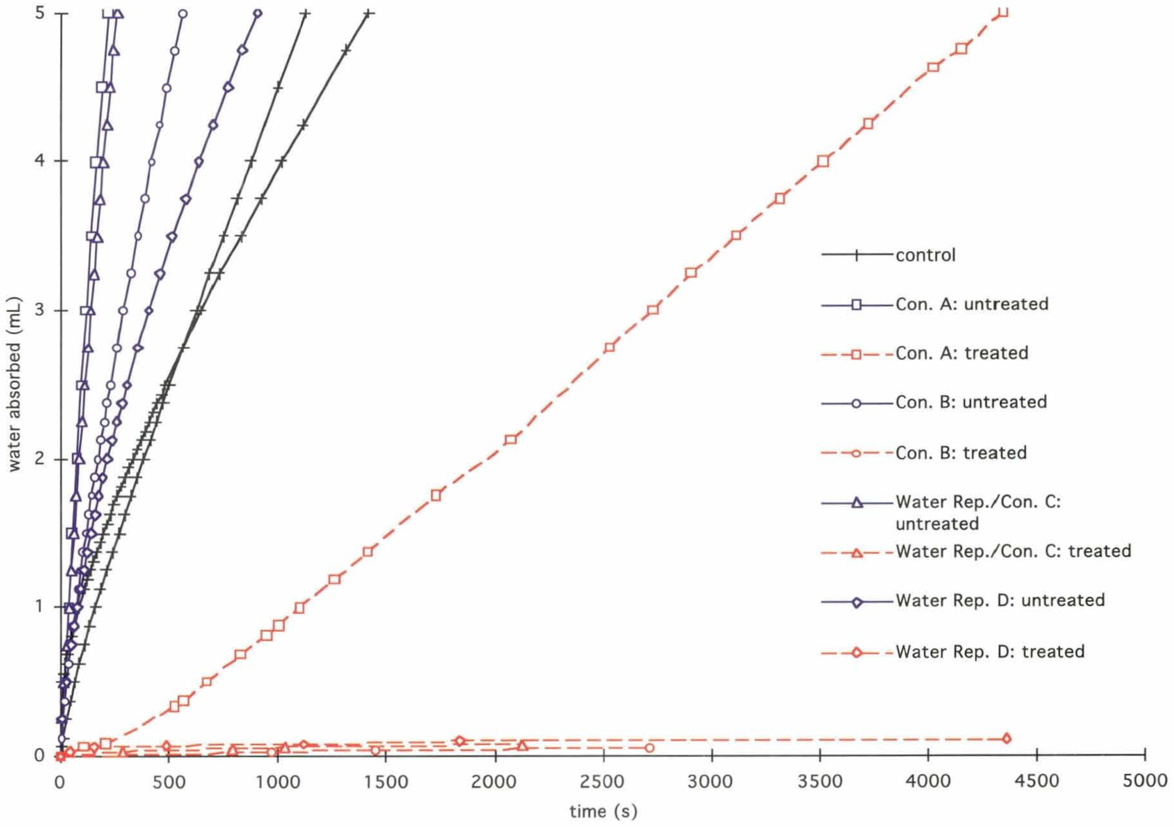


*Figure 29a Water absorption rates of **fresh Locharbriggs** sandstone samples before and after treatment with consolidants and water repellents.*

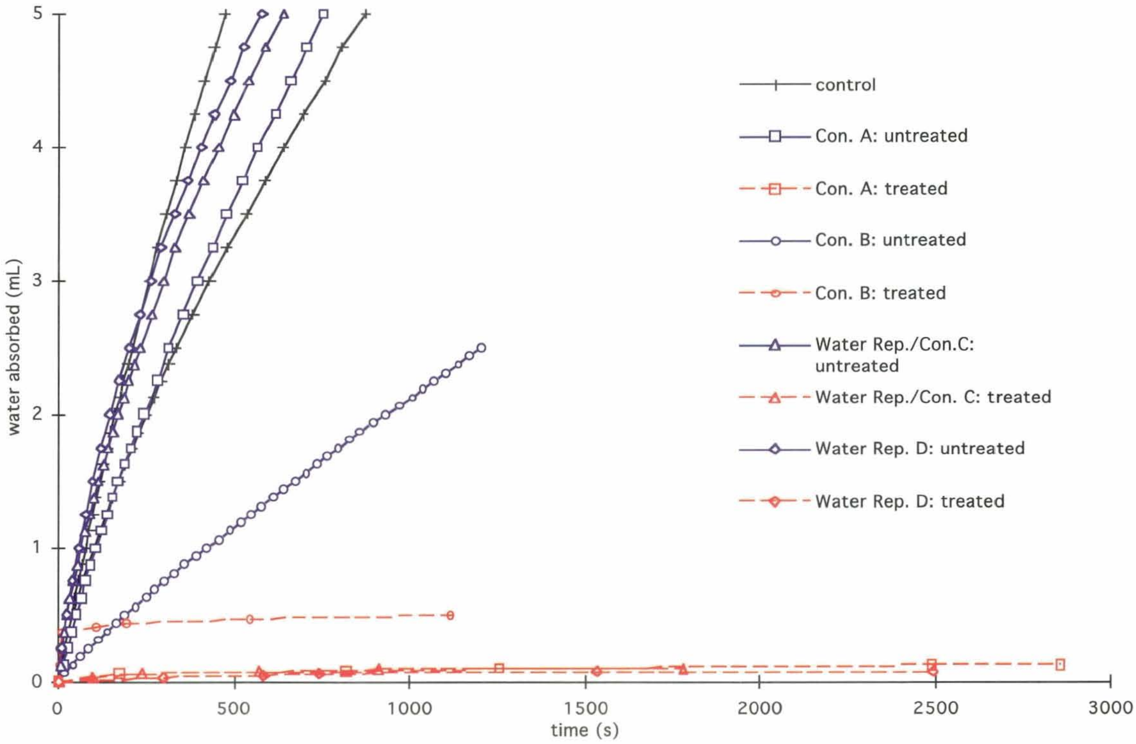


*Figure 29b Water absorption rates of **soiled Locharbriggs** sandstone samples before and after treatment with consolidants and water repellents.*

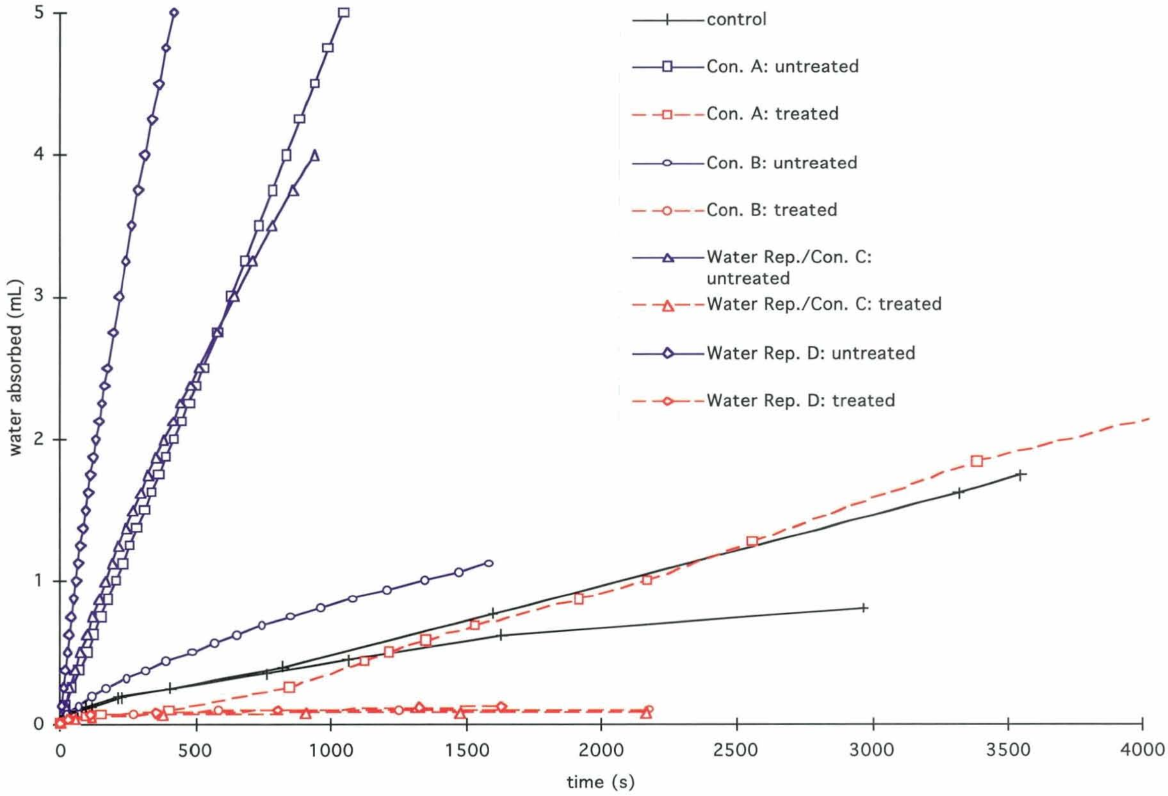


Figure 29c Water absorption rates of ***fresh Clashach*** *sandstone samples before and after treatment with consolidants and water repellents.*

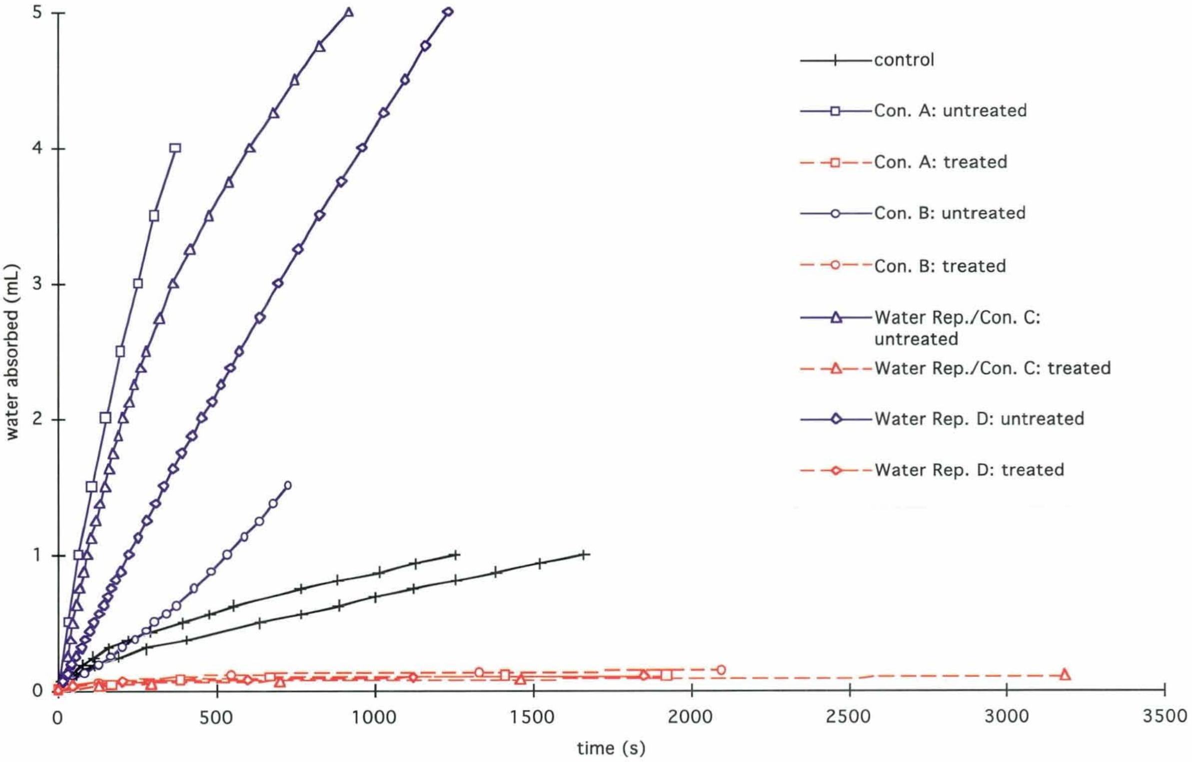


Figure 29d Water absorption rates of ***soiled Clashach*** *sandstone samples before and after treatment with consolidants and water repellents.*

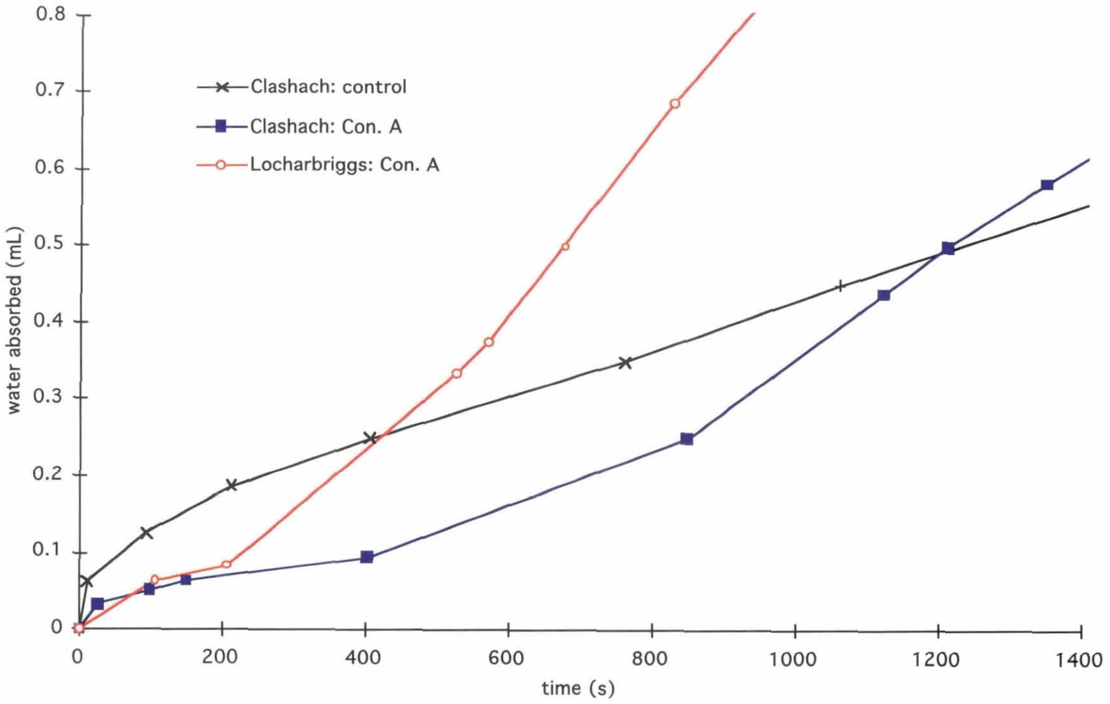


Figure 29e *Water absorption rates of* ***fresh Locharbriggs and Clashach*** *sandstone samples after treatment with Consolidant A showing the initial slow water absorption rate which speeds up later in the experiment. A typical water absorption pattern (slowing throughout measurement) is shown for comparison (Clashach: control).*

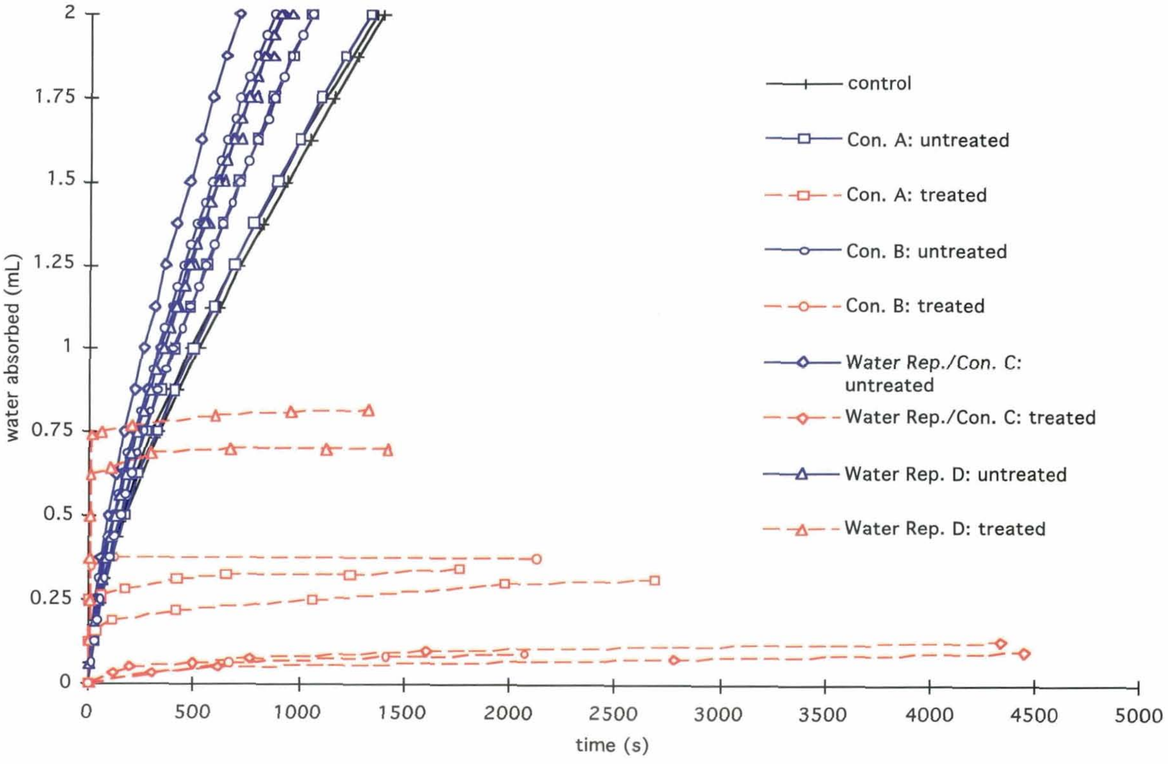


Figure 29f *Water absorption rates of fresh Stainton sandstone samples before and after treatment with consolidants and water repellents.*

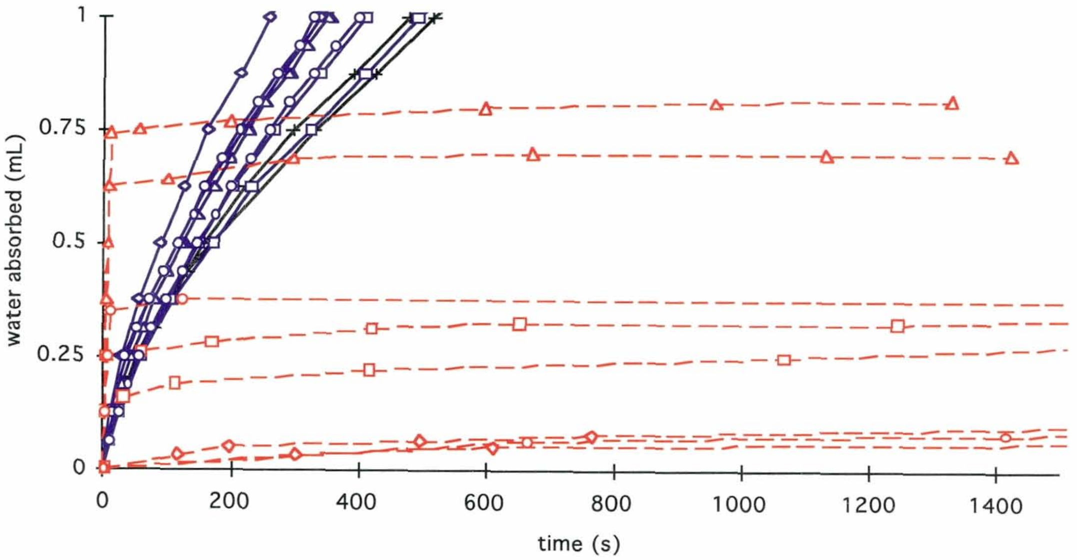


Figure 29g Magnified section from Figure 29f showing initial stages of water absorption of ***fresh Stainton*** *sandstone samples before and after treatment with consolidants and water repellents.*

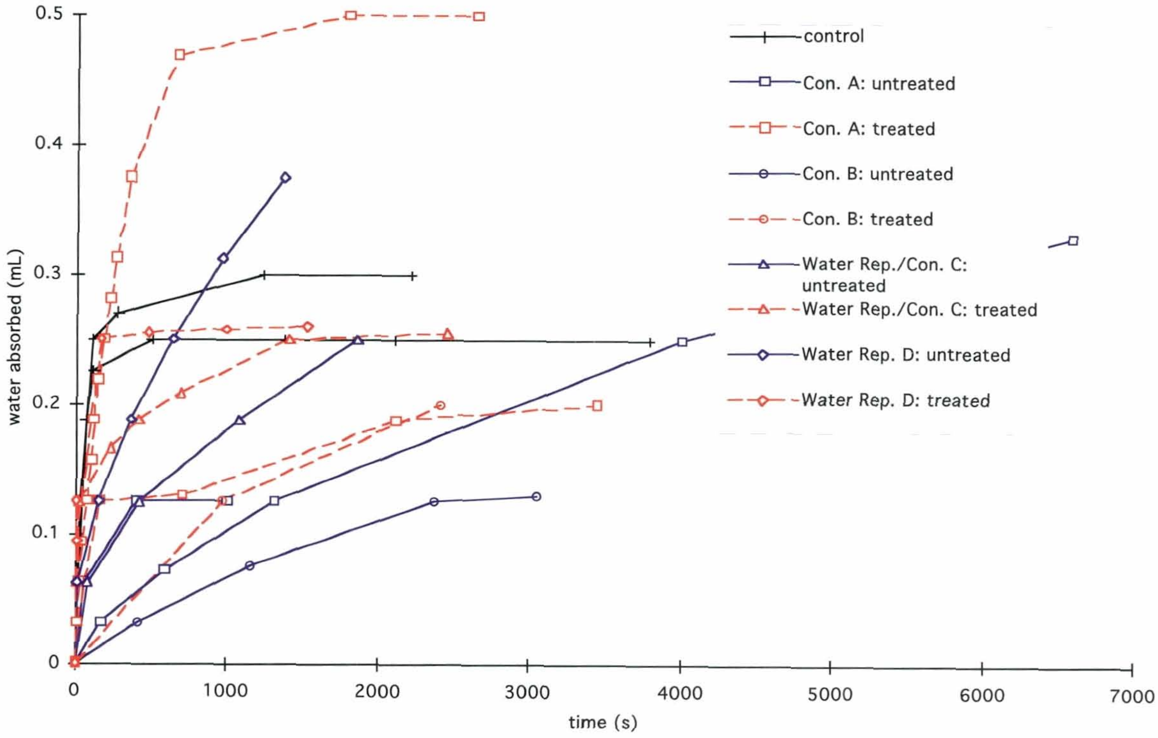


Figure 29h Water absorption rates of ***soiled "Unknown A"*** *sandstone samples before and after treatment with consolidants and water repellents.*

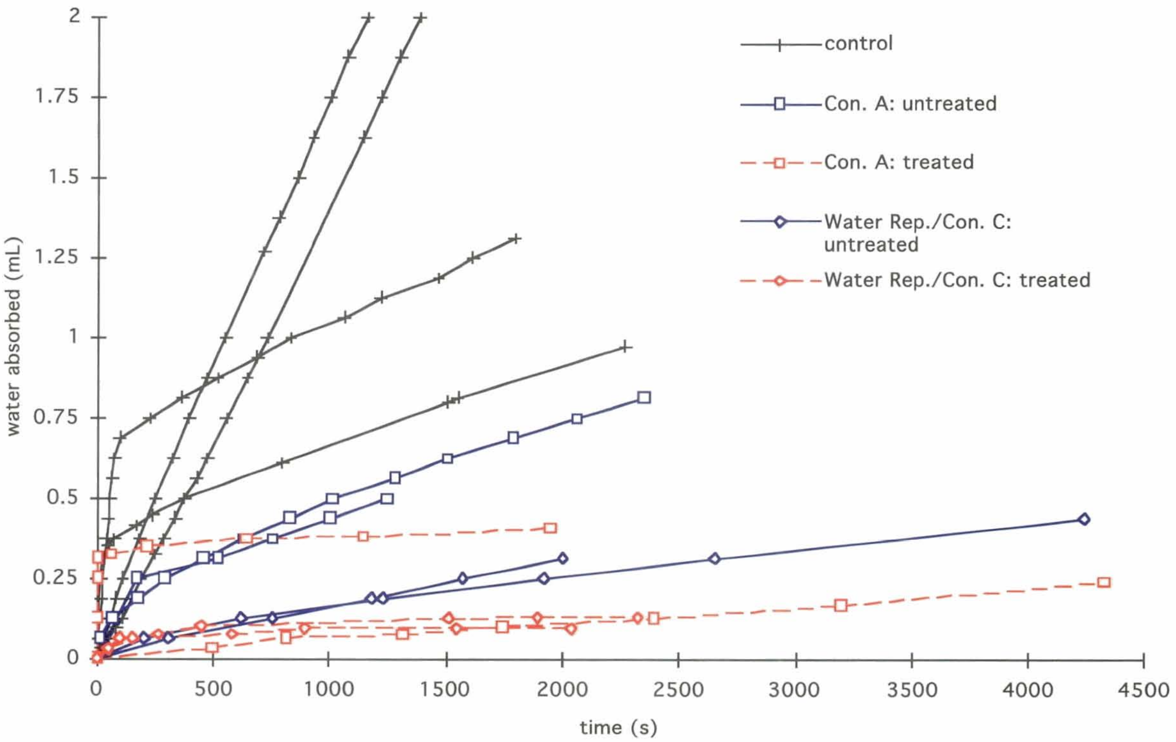


Figure 29i *Water absorption rates of* ***soiled "Unknown B"*** *sandstone samples before and after treatment with consolidants and water repellents. Panels 1, 2 & 3.*

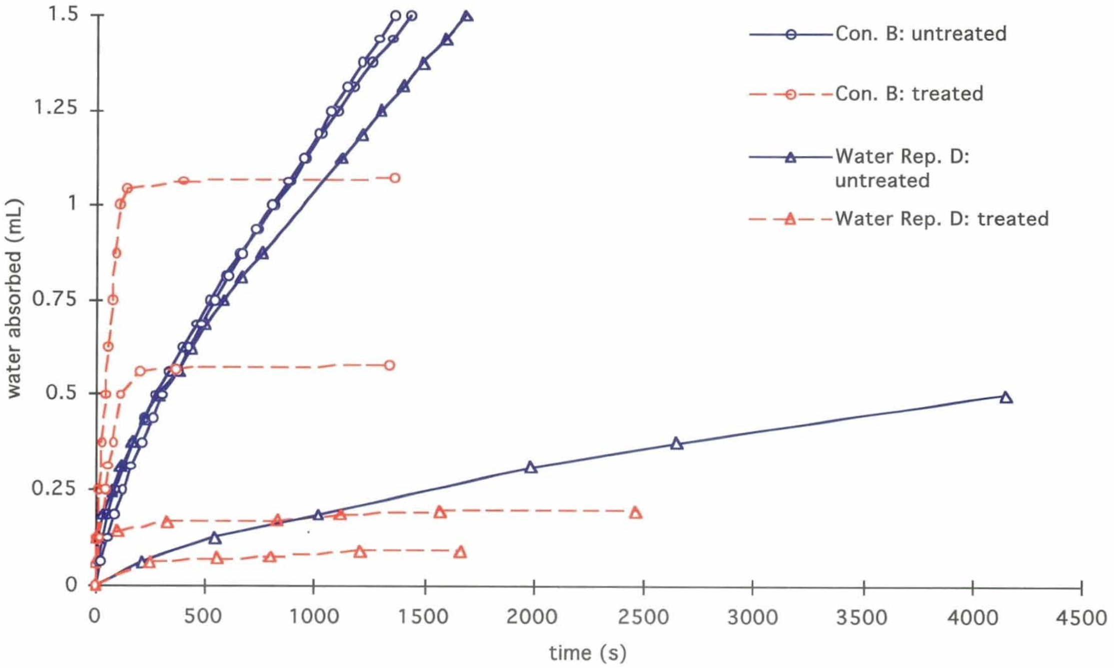


Figure 29j *Water absorption rates of* ***soiled "Unknown B"*** *sandstone samples before and after treatment with consolidants and water repellents. Panels 4 & 5.*

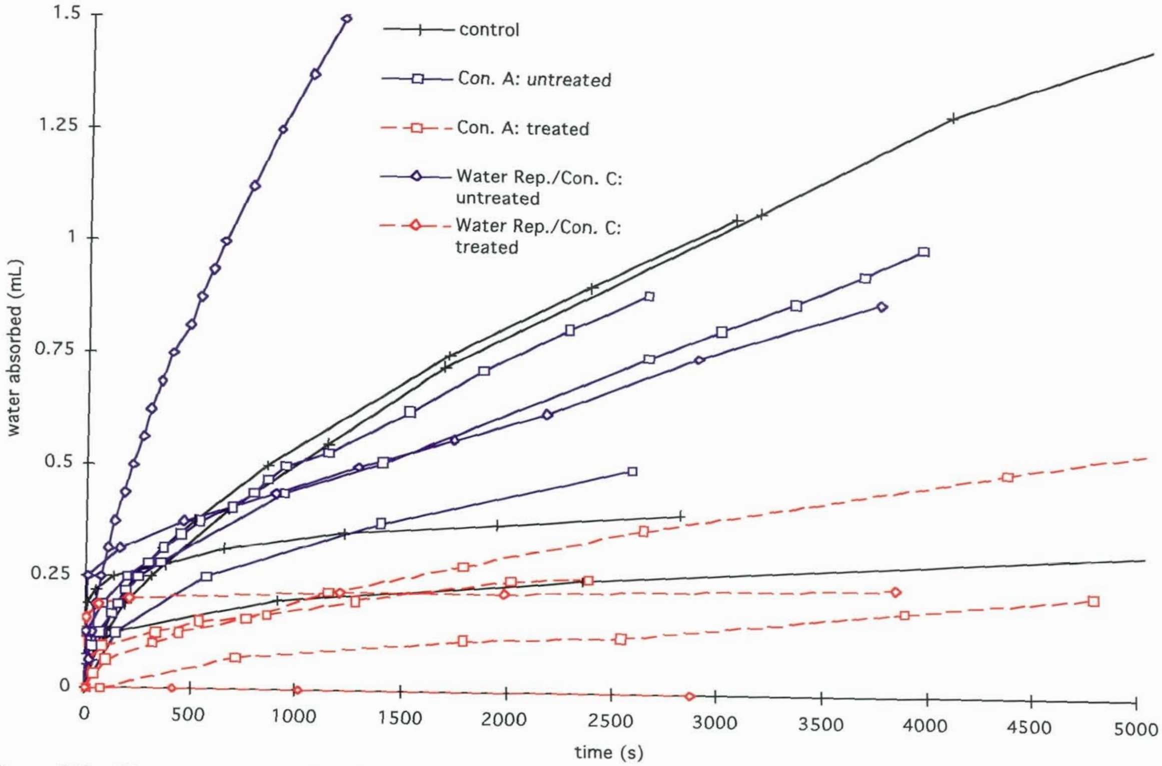


Figure 29k Water absorption rates of ***soiled Cat Castle*** *sandstone samples before and after treatment with consolidants and water repellents. Panels 1 to 3.*

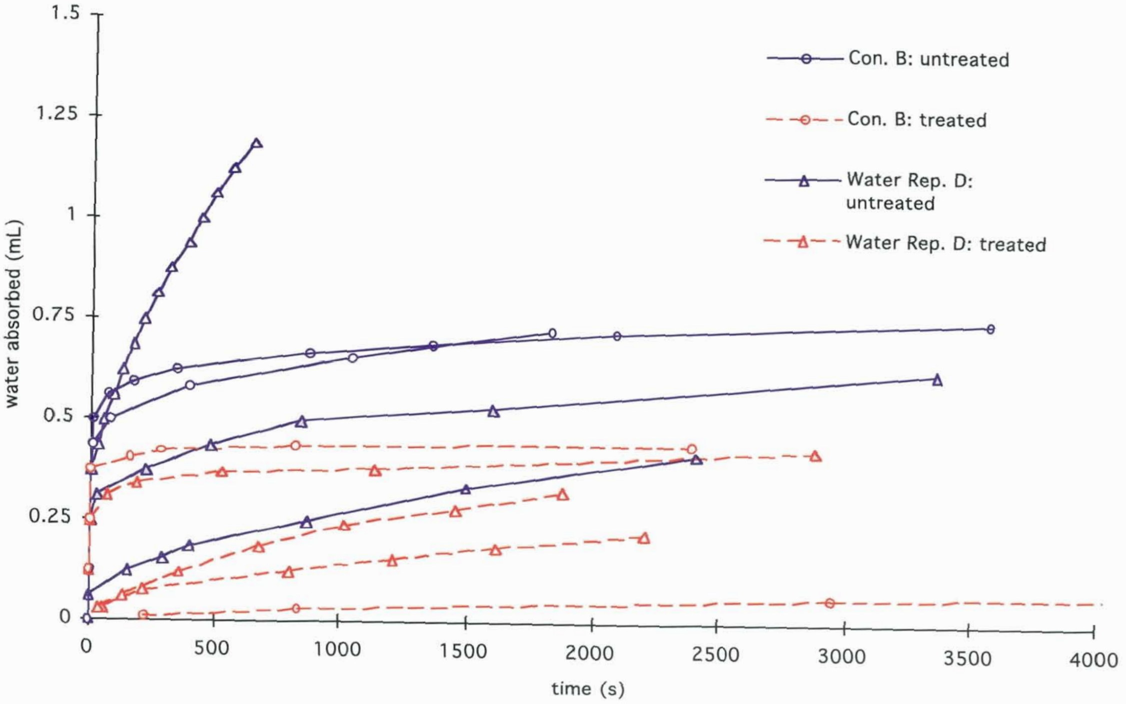


Figure 29l Water absorption rates of ***soiled Cat Castle*** *sandstone samples before and after treatment with consolidants and water repellents. Panels 4 and 5.*

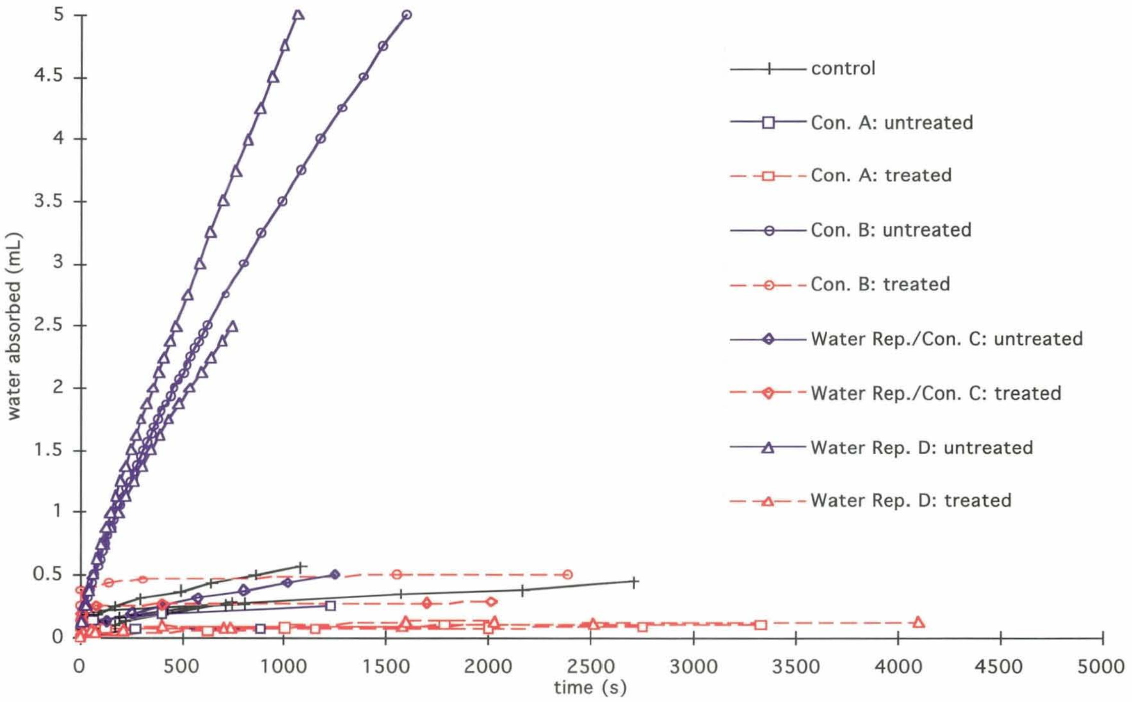


Figure 29m Water absorption rates of ***soiled "Unknown C"*** *sandstone samples before and after treatment with consolidants and water repellents.*

4.4.3 Strength tests

A selection of treated sandstones from the RGU panels was identified. The sandstones were cored to produce samples suitable for strength tests. The exact methodology is given in Section 3.2. The samples that were fresh sandstones were labelled as 'F'. The soiled and weathered sandstones were described as soiled 'S' and represented sandstones which were in varying degrees friable, weathered and soiled. The selection thus comprised:

Stone type	Label	Stone type	Label
Soiled Locharbriggs	Lo/s	Soiled Unknown B	St/s
Fresh Locharbriggs	Lo/f	Fresh Stainton	St/f
Soiled Leoch	Le/s	Soiled Clashach	Cl/s
Fresh Leoch	Le/f	Fresh Clashach	Cl/f

The following treatments were used:

Consolidant A	Water Repellent/Consolidant C
Consolidant B	Water Repellent D
Untreated control	

The sandstone cores were sliced with a diamond saw at 3 mm increments into the treated face. This created slices of thickness 2-3 mm with a diameter 20-45 mm depending on the nature of the core and surface. Ultimate strength and modulus of elasticity of each slice were measured by using the customised RILEM strength test for Ultimate Bending Strength (iii.6). The details of the test are explained in Section 3.3.1. The results were plotted against depth into treated face.

Consolidant A

There was a slight consolidation effect of Consolidant A treatment on "Unknown B" sandstone and Stainton sandstone. The four plots for strength and elasticity (Figure 30) show a possible increasing trend between 5-15 mm into the stone; however, this effect could be random as there was a large variation in all the data.

Consolidant B

Consolidant B did increase both the ultimate strength and the modulus of elasticity up to 7 mm in some stone types (the top two slices of fresh Locharbriggs, weathered Clashach, "Unknown B" and Stainton). The fresh Clashach, weathered Locharbriggs, fresh and weathered Leoch did not significantly change on application of Consolidant B.

Water Repellent D and Water Repellent/Consolidant C

No consolidation was observed for Water Rep./Con. C and Water Repellent D. Water Rep./Con. C is a water repellent and so would not be expected to show consolidation.

There were no consolidants that increased the sub-surface strength of sandstone. The control samples showed weakening in the top increment (outer surface). This could be because of weathering, or because the surface of the first increment is subject to non-circular shape, scratches, curves or pitting from the original cutting of the block or weathering. However several of the treated soiled samples did not show a similar surface drop in strength. Thus some treatments could appear to "hold together" the top layer, but not significantly increase the strength or elasticity of the masonry beyond that of the untreated material. Essentially some consolidants can support the weathered layer, but not alter the inherent structural failures in the weathered stone.

The failure to determine any outstanding increases in strength with Consolidant A and Water Rep./Con. C shows that either there is no consolidation effect, or that the difference produced by the treatments is masked by the variation in strength and elasticity of the stones. In either case if both do not increase the strength beyond the natural variation found in the masonry then very little consolidation occurred. Additionally BRE experience from previous consolidant projects has shown that laboratory samples treated with consolidants tend to become very dense and hard, and almost vitrified on re-treatment. However, the treatments used in this project show little strength increase on the panels even although the treatments were applied until saturation. The difference is possibly that the treatments applied to the panels are uncontrolled on one side of the masonry. This allows the treatment to subsequently absorb to a depth were it becomes too dilute to have a strengthening effect. In laboratory samples the applicator would apply the treatments till saturation on a small sample and this could allow a laboratory sample to become completely impregnated with the treatment. In addition it may also be that a surface blocking effect by partially solidified consolidant causes saturation to be reached too quickly in the treated panels.

4.4.4 Depth and distribution by water absorption

The treatments used generally increased the hydrophobicity (water repellency) of stone masonry. Thus water is a useful method of detecting the existence or location of treatments. Three different water based tests were carried out to determine the depth and distribution of treatments (Section 3.3.2). Although one of the treatments (Consolidant A) was designed as a hydrophilic consolidant, its early stages in application are still hydrophobic and allows its detection.

4.4.4.1 RILEM (ii.8b) based water drop tests

The time taken to absorb water is recorded to generally locate the depth of penetration (Section 3.3.2). More comprehensive RILEM tests were carried out to show the change in hydrophobicity as Consolidant A cured. The effects of wetting and drying can also be used to locate treatments.

Selection of sandstones and treatments

A selection of treated sandstones from the RGU panels were identified. The sandstones were cored to produce samples suitable for tests. The exact methodology is stated in Section 3.2. The samples which were fresh sandstones were labelled as 'F' . The soiled and weathered sandstones were described as soiled 'S'. The selection comprised:

Stone type	**Label**	**Stone type**	**Label**
Soiled Locharbriggs	Lo/s	Soiled Unknown B	St/s
Fresh Locharbriggs	Lo/f	Fresh Stainton	St/f
Soiled Leoch	Le/s	Soiled Clashach	Cl/s
Fresh Leoch	Le/f	Fresh Clashach	Cl/f

The following treatments were used:

Consolidant A	Water Repellent/Consolidant C	Untreated control
Consolidant B	Water Repellent D	

Results were recorded in terms of minimum, maximum and average depth of penetration (Table 9). A substantial number of zero values were recorded for depth of penetration on some cores. This is unlikely to be the case as the application methods and volumes were consistently carried out and well documented. It is more likely that the treatment only penetrated a few millimetres, or had become too diluted.

Consolidant A is a marketed as hydrophilic consolidant. It however does show hydrophobic nature. Changes in water drop test results for Consolidant A treatment determined that its initial hydrophobic nature would slowly change to hydrophilic over a period of months.

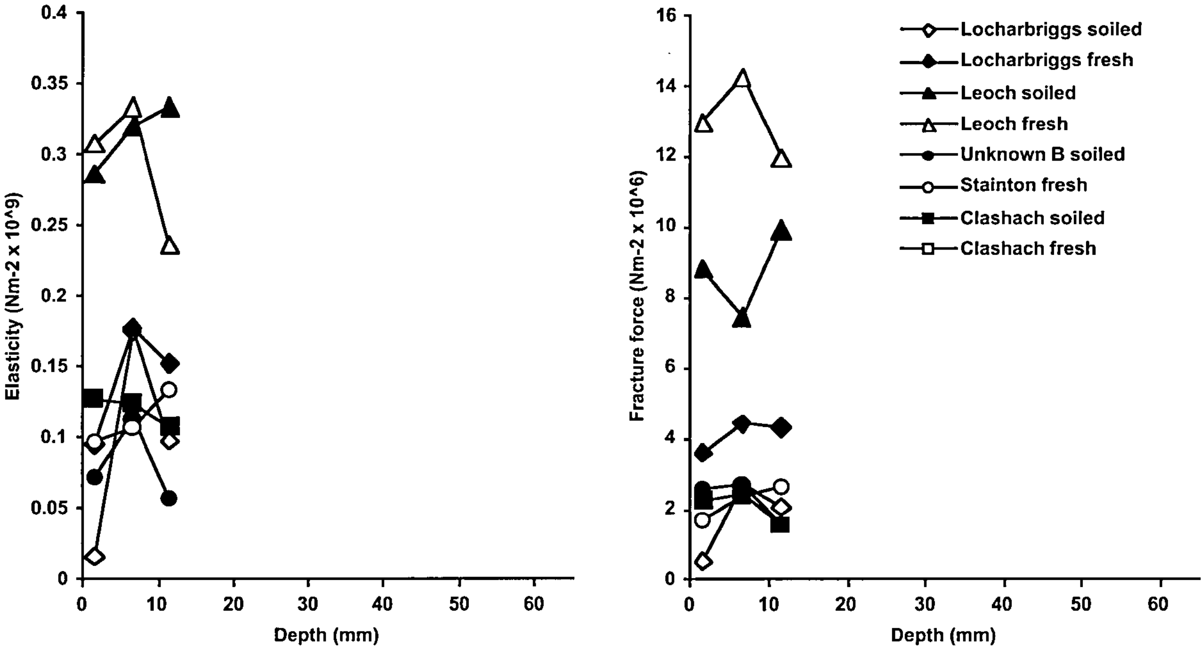


Figure 30a Elasticity (Nm^{-2} X 10^9) and fracture force (Nm^{-2} X 10^6) of the untreated sandstones at different depths into the surface.

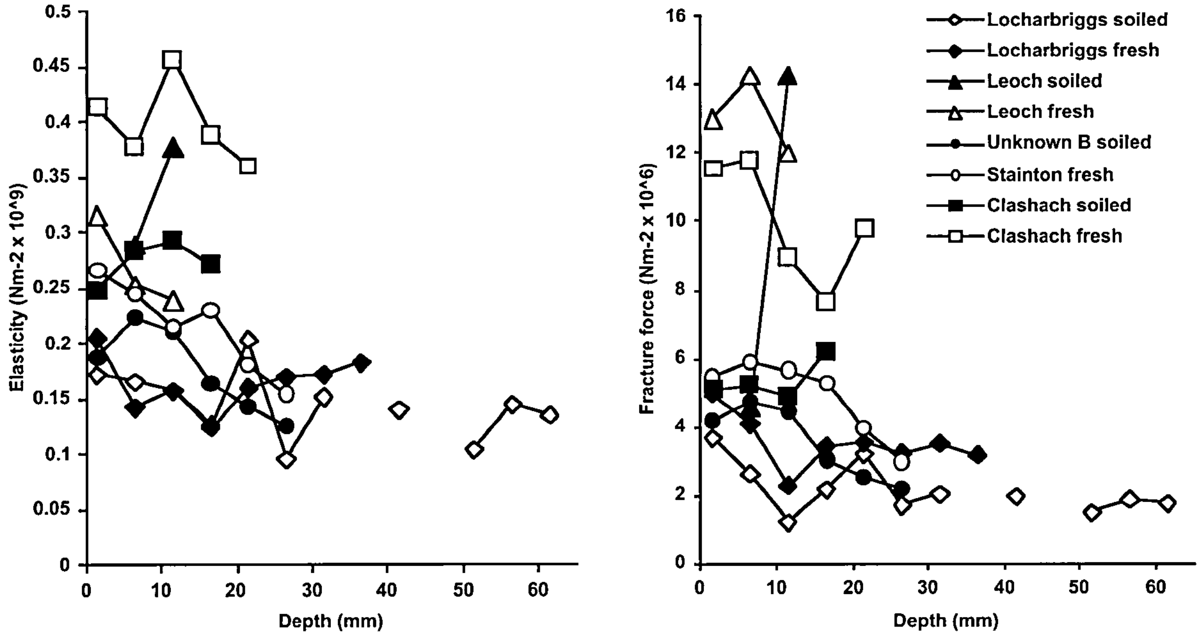


Figure 30b Elasticity (Nm^{-2} X 10^9) and fracture force (Nm^{-2} X 10^6) of the Consolidant A treated sandstones at different depths into the surface.

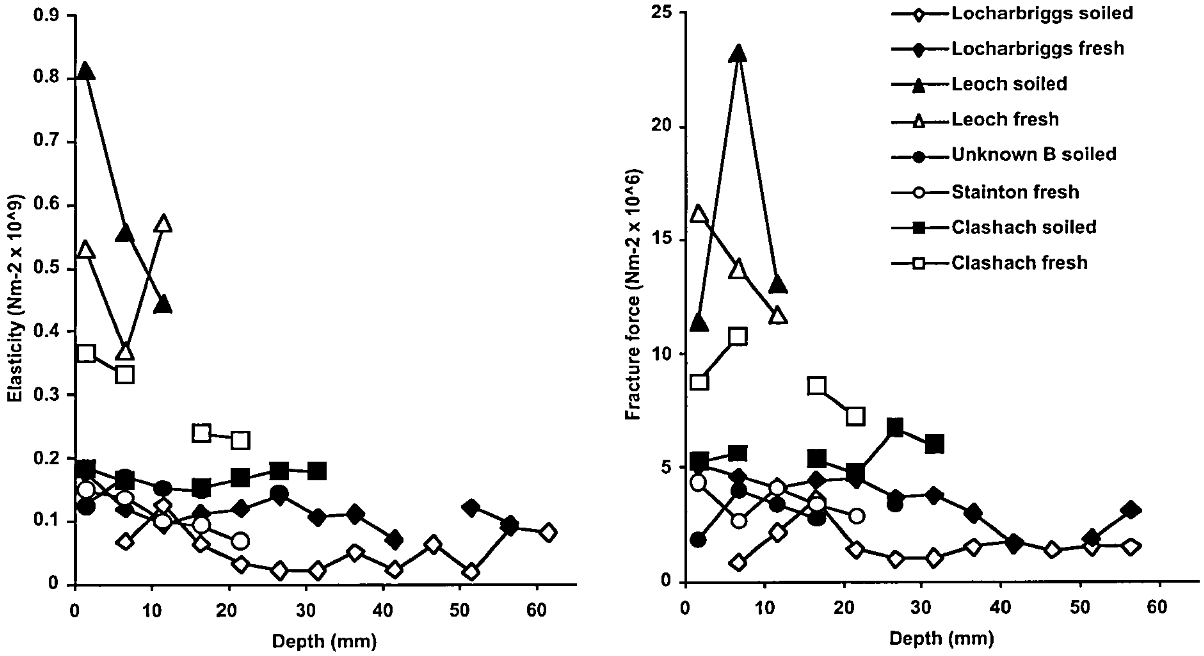


Figure 30c Elasticity (Nm^{-2} X 10^{9}) and fracture force (Nm^{-2} X 10^{6}) of the Water Repellent / Consolidant C treated sandstones at different depths into the surface.

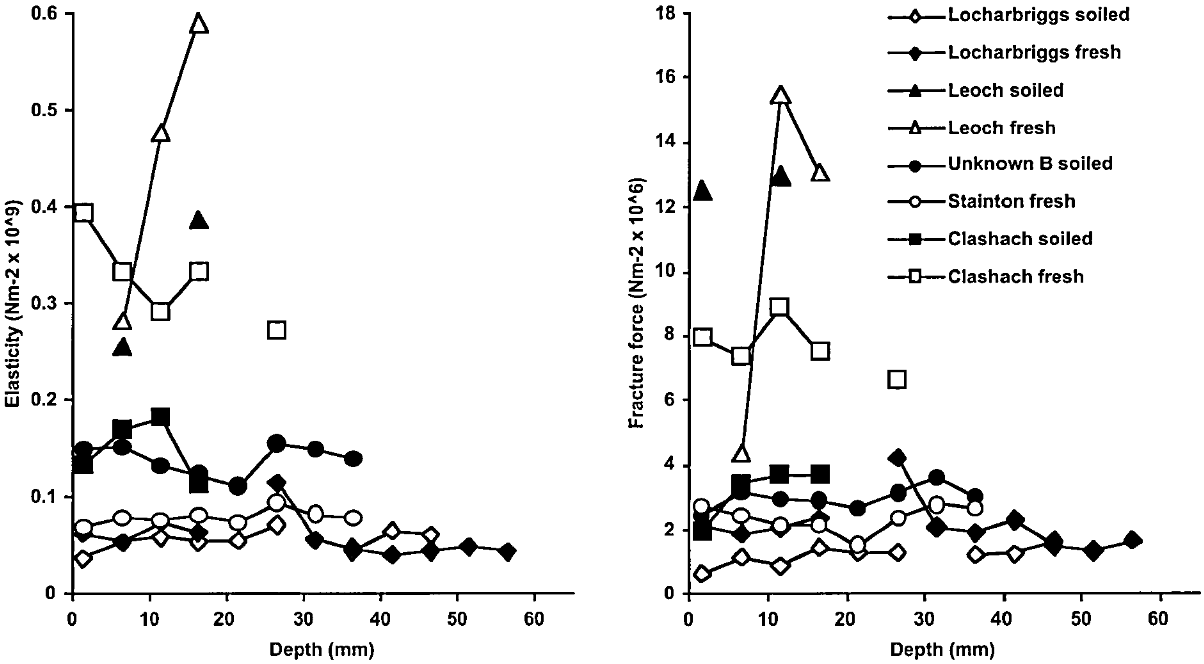


Figure 30d Elasticity (Nm^{-2} X 10^{9}) and fracture force (Nm^{-2} X 10^{6}) of the Water Repellent D treated sandstones at different depths into the surface.

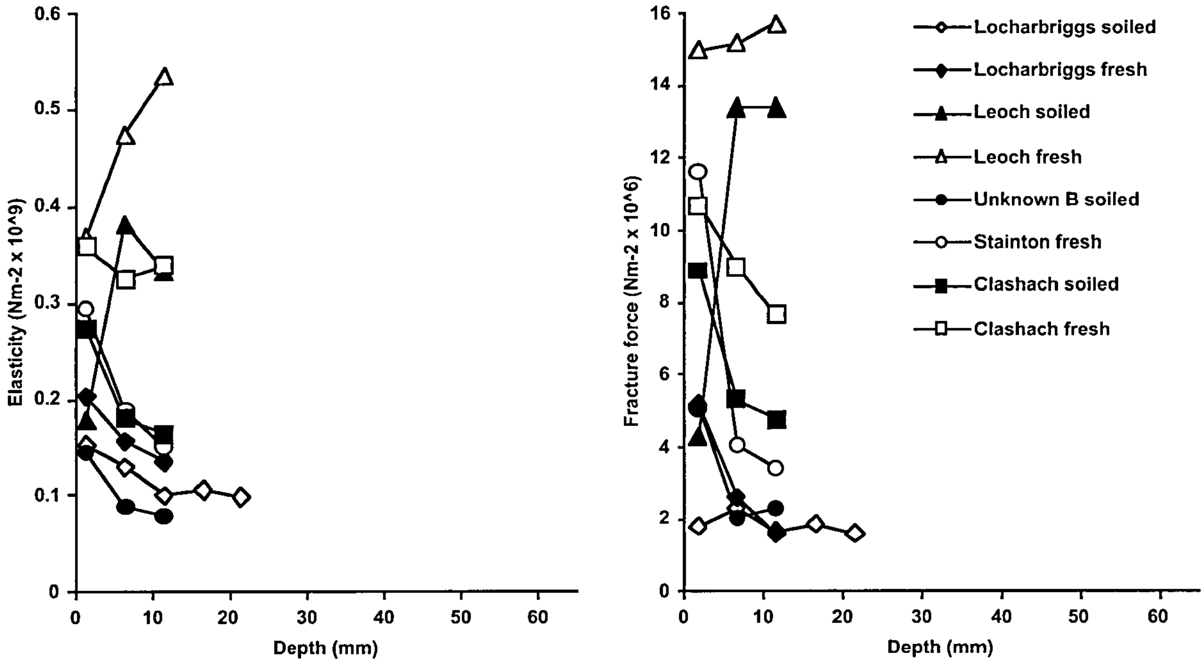


Figure 30e Elasticity (Nm^{-2} X 10^9) and fracture force (Nm^{-2} X 10^6) of the Consolidant B sandstones at different depths into the surface.

	Consolidant A			Consolidant B			Water Repellent / Consolidant C			Water Repellent D		
Stone	lower	upper	**mean**	lower	upper	**mean**	lower	upper	**mean**	lower	upper	**mean**
Lo/s	20	50	**30**	5	10	**7**	30	60	**44**	25	60	**39**
Lo/f	0	60	**27**	5	20	**12**	25	50	**39**	50	60	**56**
Le/s	0	0	**0**	0	0	**0**	0	5	**0**	0.5	5	**4**
Le/f	0	0	**0**	0	0	**0**	0	0	**0**	0	0.5	**0**
St/s	5	10	**8**	0	< 0.5	**< 0.5**	20	40	**26**	15	20	**17**
St/f	0	5	**5**	0	0.5	**0**	5	30	**21**	10	15	**13**
Cl/s	0	0	**0**	0	5	**1**	20	30	**24**	0	25	**15**
Cl/f	0	0.5	**0**	0	0.5	**0**	15	30	**18**	5	10	**10**

Table 9 Depth of penetration (mm) of treatments by RILEM based test.

4.4.4.2 Change in hydrophobicity test

A core taken from the Locharbriggs sandstone panel treated with Consolidant A was stored for 7 months. The core was cut lengthways in half and dried for two days. The change in hydrophobicity test methodology described in Section 3.3.5.2 was then used. RILEM based water drop tests were carried out to compare the hydrophobic nature of the outside of the core to the freshly cut inside of the core. The results are plotted in Figure 31. The figures show that in the freshly cut core there are two hydrophobic layers at 3.5-4.5 cm and at 0.5-0 cm. There is also an intermediary zone where all hydrophobicity has vanished. The core stored for 7 months has lost all surface hydrophobicity.

These results show that the hydrophobic nature of surfaces treated with Consolidant A disappeared over a period of months and became hydrophilic. The results of the RILEM test immediately after coring treated surfaces are therefore very different to those found after several months. This implies that there is a hydrophobic component to Consolidant A which remains for a period of time, but slowly evaporates away or becomes hydrophilic. This effect however only occurs on the surface. Freshly cut cores, which were treated 7 months previously, still showed two hydrophobic layers at 3.5-4.5 cm into the surface, and at 0-0.5 cm. Therefore sub-surface hydrophobicity remains for over 7 months at a depth of 3-4 cm, and in a fine subsurface layer less than 0.5 mm with Consolidant A.

The two layers of hydrophobic nature can be explained by the following theory. After application of the consolidant the volatile solvent used (in this case ethyl methyl ketone) begins to evaporate or move by capillary action. The movement of solvent occurs both towards the surface of the masonry panel to air and into the untreated area of masonry, deeper in the stone. Evaporation and capillary action can allow separation of organic compound mixtures. As a result the solvent selectively draws different consolidant components into and out of the stone. The consolidant at a partially consolidated phase may contain a range of different compounds with different hydrophobicity. On final evaporation there are concentrations of more hydrophobic compounds.

Hydrophilic treatments are not easily detectable using the RILEM based water tests and give variable results. However, hydrophilic treatments can still be hydrophobic under the surface for over 7 months after treatment.

4.4.4.3 Wetting and drying effect tests

The effects of wetting and drying were used to locate the existence and distribution of hydrophobic treatments. The methodology is described in Section 3.3.5.3. The test consisted of "splashing" cores with water and observing the areas that appear dry or wet. Subsequently the cores were soaked in water for 10 seconds and left to dry. The hydrophobic regions dry more quickly than the untreated areas.

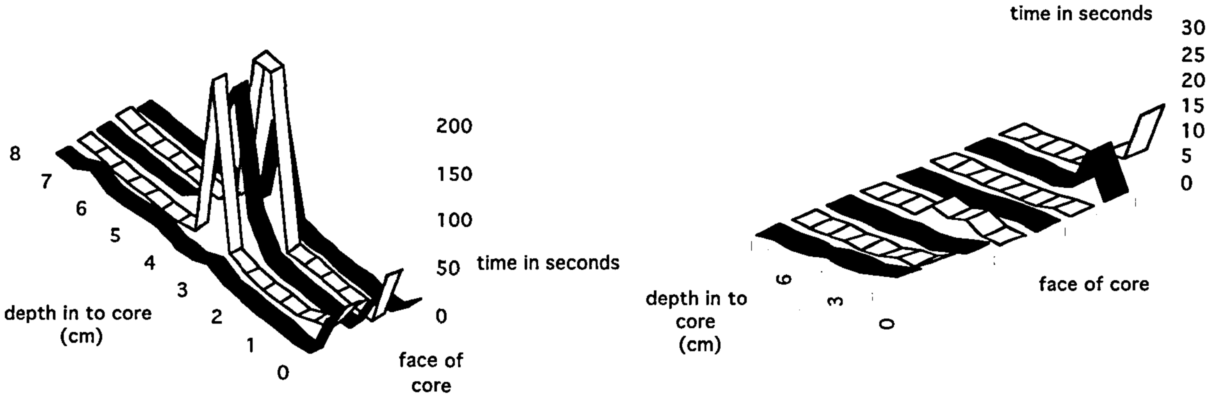


Figure 31 Change in hydrophobic nature of Consolidant A. The lower graph is the results of water drop tests on the outside of a core of Locharbriggs sandstone after storage for 7 months. The top graph is the results on the freshly cut inside of a core.

Selection of sandstones and treatments

A selection of treated sandstones from the RGU panels were identified. The sandstones were cored. The exact methodology is stated in Section 3.2. The samples which were fresh sandstones were labelled as 'F'. The soiled and weathered sandstones were described as soiled 'S'. The selection comprised:

Stone type	Label	Stone type	Label
Soiled Locharbriggs	Lo/s	Soiled Unknown B	St/s
Fresh Locharbriggs	Lo/f	Fresh Stainton	St/f
Soiled Leoch	Le/s	Soiled Clashach	Cl/s
Fresh Leoch	Le/f	Fresh Clashach	Cl/f

The following treatments were used:

Consolidant A	Water Repellent/Consolidant C
Consolidant B	Water Repellent D
Untreated control	

Consolidant A, Consolidant B, Water Rep./Con. C and Water Repellent D were all detectable with this method. Results are shown in Table 10. Figures 32 to 34 show photographs of some of the results. Note the difference between the effects of Consolidant A upon drying (Figure 32) and wetting (Figure 33). The results of the drying tests were more visible if flat cut surfaces were used rather than the sides of the cores. Drying samples in an oven at 70°C did not appear to change the results significantly.

Depths of penetration calculated via this method are not consistent with RILEM based tests (Tables 9 & 10). There is also a substantial difference between wetting and drying results for depth of penetration. Therefore the results of consolidation depth of penetration tests based on water hydrophobicity are only a rough guide, and cannot be guaranteed to produce results.

This test is very useful as a preparation for any RILEM based water drop tests. It quickly shows where to look for the consolidant. Additionally where the consolidant was not detected by wetting, it could often be detected by drying and vice versa.

	Consolidant A		Consolidant B		Water Repellent / Consolidant C		Water Repellent D	
Stone	**wetting**	**drying**	**wetting**	**drying**	**wetting**	**drying**	**wetting**	**drying**
Lo/s	40/35	29/28	16/5	unclear	39/38	39/38	48/27	unclear
Lo/f	50/46	36/35	7/6	unclear	30/22	30/22	24/21	unclear
Le/s	0/0	0/0	0/0	0/0	0/0	0/0	0.5/0	unclear
Le/f	0/0	0/0	0/0	0/0	0/0	0/0	4/2	unclear
St/s	0/0	17/15	0/0	4/4	36/17	unclear	9/8	unclear
St/f	0/0	30/20	0/0	2/2	26/22	unclear	12/14	unclear
Cl/s	0/0	30/15	7/2	unclear	unclear	43/40	25/18	unclear
Cl/f	0/0	25/15	7/2	unclear	11/11	unclear	18/14	unclear

Table 10 Maximum and minimum depths of penetration (mm) of consolidant.

Figure 32 The effects of drying on Consolidant A treated Clashach, Unknown B and Stainton sandstones which had been soaked in water for 10 seconds.

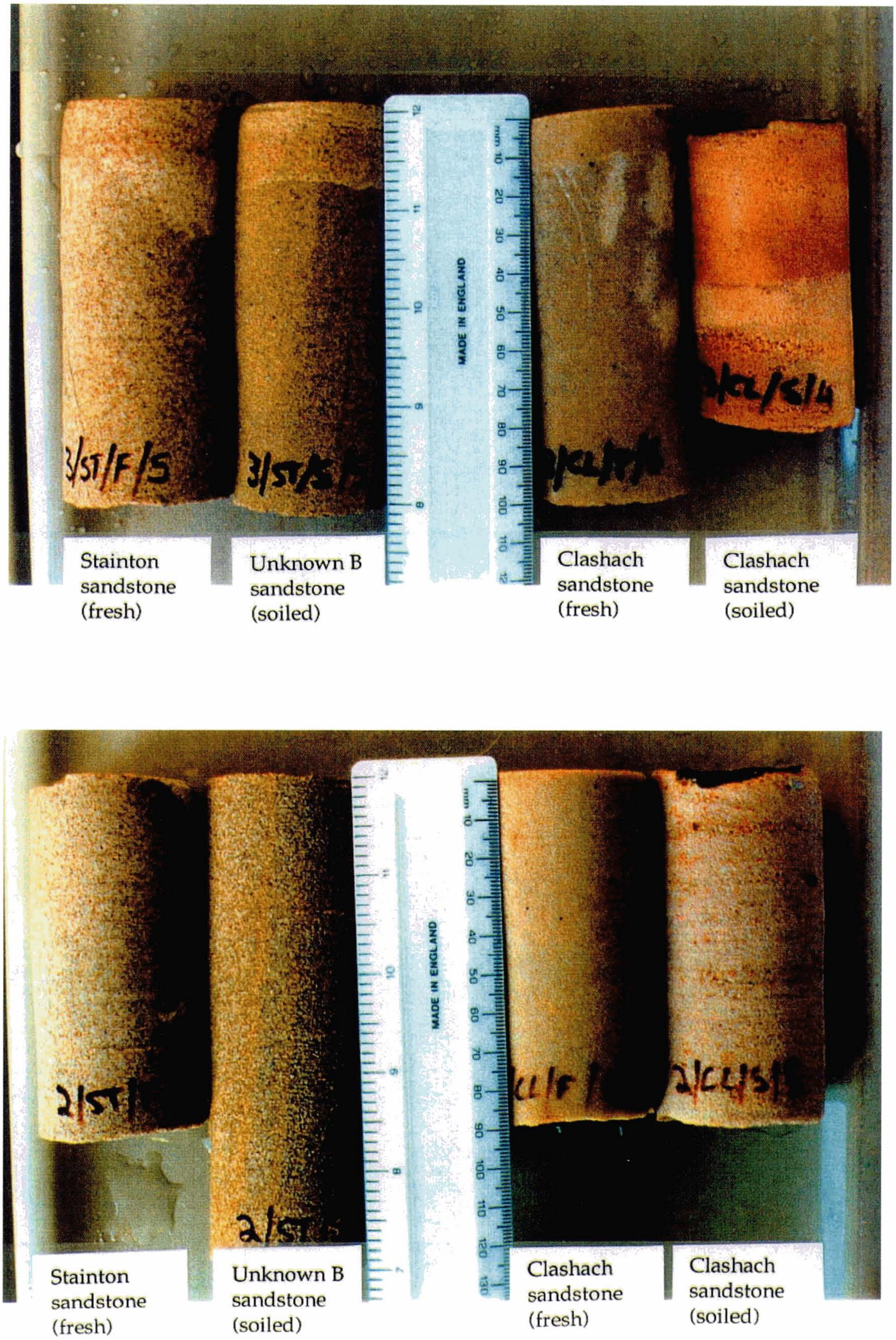


Figure 33 The effects of water wetting on treated sandstone cores. Top: Water Rep./Con. C on Stainton, Unknown B and Clashach. Bottom: Consolidant A on Unknown B, Stainton and Clashach.

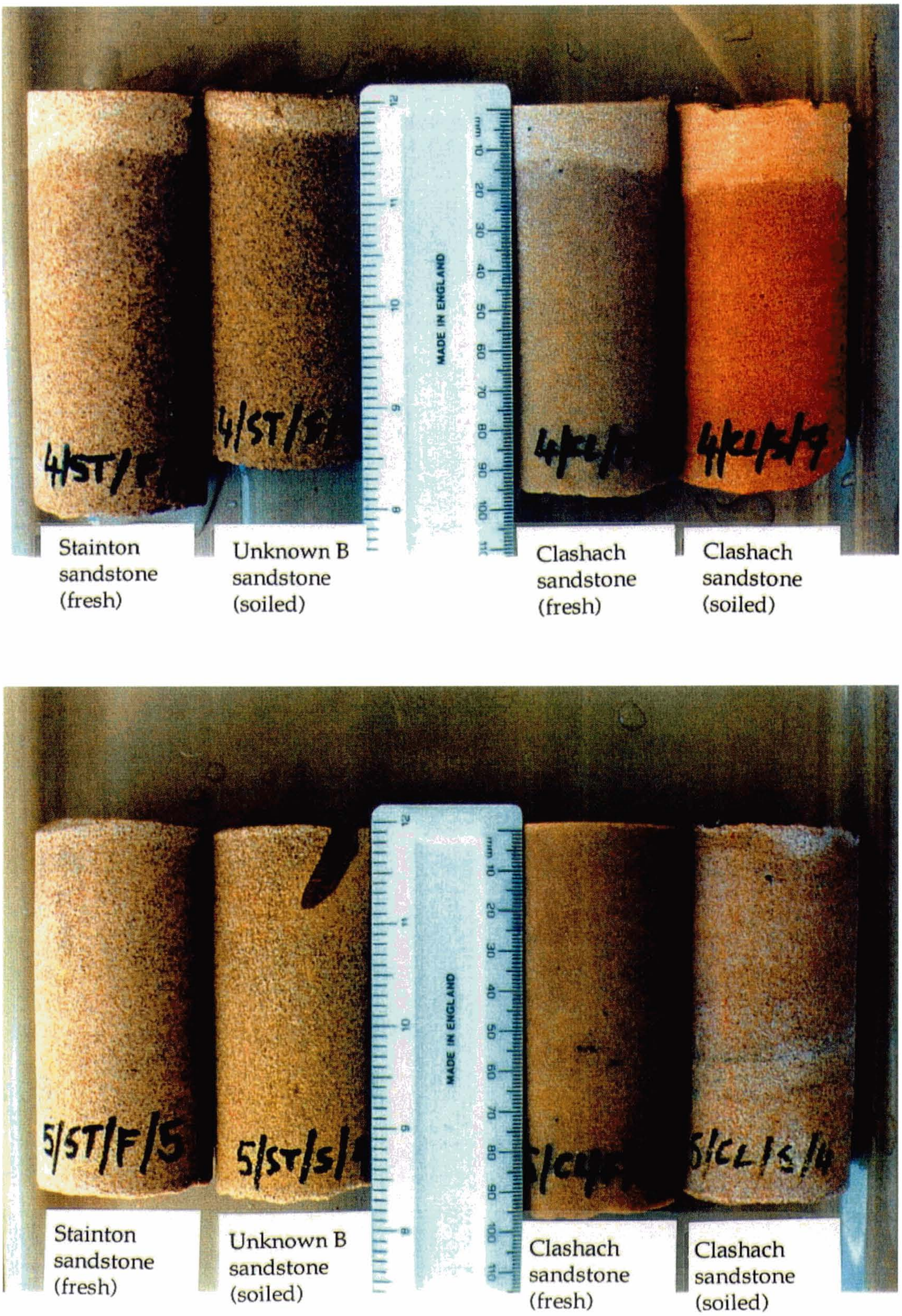


Figure 34 The effects of drying on treated sandstone cores. Top: Water Repellent D on Stainton, Unknown B and Clashach. Bottom: Consolidant B on Unknown B, Stainton and Clashach.

Both the stone type and the treatment type strongly influenced the depth of penetration. Taking into account all the current testing the following treatment depths of penetration can be suggested:

Consolidant A, Water Rep./Con. C and Water Repellent D

Clashach, "Unknown B" and Stainton sandstones absorbed the treatments to about 15-30 mm. Locharbriggs sandstone absorbed to about 30-60 mm. Leoch sandstone absorbed Water Repellent D to about 5 mm into the weathered layers only.

Consolidant B

The consolidant consistently penetrated to about 7 mm into Locharbriggs sandstone, and about 2 mm into Stainton, "Unknown B" and Clashach. Zero in Leoch sandstone.

Weathered surface layers did not inhibit the depth of penetration in "sound" stone beneath the friable surface. Any friable surface layers would easily pick up the treatments. Bedding planes that were detected could occasionally be observed to distort the absorption of treatments (mostly Locharbriggs) or cause tracking of the treatments (illus 74).

A range of water based tests were required to detect these treatments in addition to RILEM based tests. This was because the depths of penetration measured by the different water based methods varied significantly. The degree of hydrophobicity of at least one of the treatments varied depending on the depth of treatment. This could be a result of uneven consolidation reactions combined with solvent evaporation.

The hydrophilic (water liking) nature of cured Consolidant A may only occur at the very surface of treated area, and take several months to occur. Such treatments can still produce a strongly hydrophobic effect within the stone, especially at the base of the consolidated zone.

4.4.5 Water vapour permeability

Consolidants may be designed with hydrophilic or hydrophobic properties depending on the required use. However, a desirable characteristic of such treatments is that they still allow water vapour to pass in and out of the stone surface. To test the water vapour transmission of treated sandstones water vapour permeability tests were carried out. The exact test is detailed in Section 3.3.6. The test involves measuring the rate of water vapour passing through slices of stone. From each stone and treatment type several slices were assessed, cut at 1 cm increments in to the treated face. This produces a depth profile of permeability effects.

Selection of sandstones and treatments

A selection of treated sandstones from the RGU panels was identified. The sandstones were cored to produce samples suitable for strength tests. The exact methodology is stated in Section 3.2. The samples that were fresh sandstones were labelled as 'F'. The soiled and weathered sandstones were described as soiled 'S'. The selection comprised:

Stone type	Label	Stone type	Label
Soiled Locharbriggs	Lo/s	Soiled Unknown B	St/s
Fresh Locharbriggs	Lo/f	Fresh Stainton	St/f
Soiled Leoch	Le/s	Soiled Clashach	Cl/s
Fresh Leoch	Le/f	Fresh Clashach	Cl/f

The following treatments were used:

Consolidant A	Water Repellent/Consolidant C
Consolidant B	Water Repellent D
Untreated control	

The following figures (Figure 35) show the results in grams of water vapour transmitted per metre square per day per centimetre sample thickness (g m^{-2} day^{-1} cm^{-1}). This is effectively the velocity of water passing through each 1 cm thick sample. Each figure compares soiled/weathered to fresh surfaces for each stone and treatment type. The results show that all four treatments reduced the water vapour permeability in the surface layers. A weathered surface condition did not significantly effect results.

The scales on plotted results have been carefully adjusted to allow easy comparison of all the data from the point of view of different treatments. However the different sandstones have very different water vapour permeabilities, and so cross comparison between the stone types cannot be so easily made. The water vapour permeability Locharbriggs was 10 times more permeable than Leoch. Changing the results to percentage change would make the data generally more comparable, however trends are best observed in the way the data is currently plotted.

The results show a general drop in water vapour permeability towards the surface of the treated cores for the different treatments. This can be observed by looking at the general trend for each stone core. The control cores do not show any general trend.

4.4.6 Exposure tests

4.4.6.1 Accelerated UV tests

Accelerated UV tests were carried out as stated in Section 3.3.7.1 on the treated faces of sandstone samples.

Selection of sandstones and treatments

A selection of treated sandstones from the RGU panels were identified. The sandstones were cored. The treated surface of each core was removed for accelerated UV testing. The exact methodology is stated in Section 3.2. The samples that were fresh sandstones were labelled as 'F'. The soiled and weathered sandstones were described as soiled 'S'. The selection comprised:

Stone type	Label	Stone type	Label
Soiled Locharbriggs	Lo/s	Soiled Unknown B	St/s
Fresh Locharbriggs	Lo/f	Fresh Stainton	St/f
Soiled Leoch	Le/s	Soiled Clashach	Cl/s
Fresh Leoch	Le/f	Fresh Clashach	Cl/f

The following treatments were used:

Consolidant A	Water Repellent/Consolidant C
Consolidant B	Water Repellent D

After 2000 hours of exposure the samples were photographed. Figure 36 shows the photographs of the exposed surfaces which sustained an appearance change. On each sample the right half of each exposed surface was masked from the UV radiation to give a control to the test.

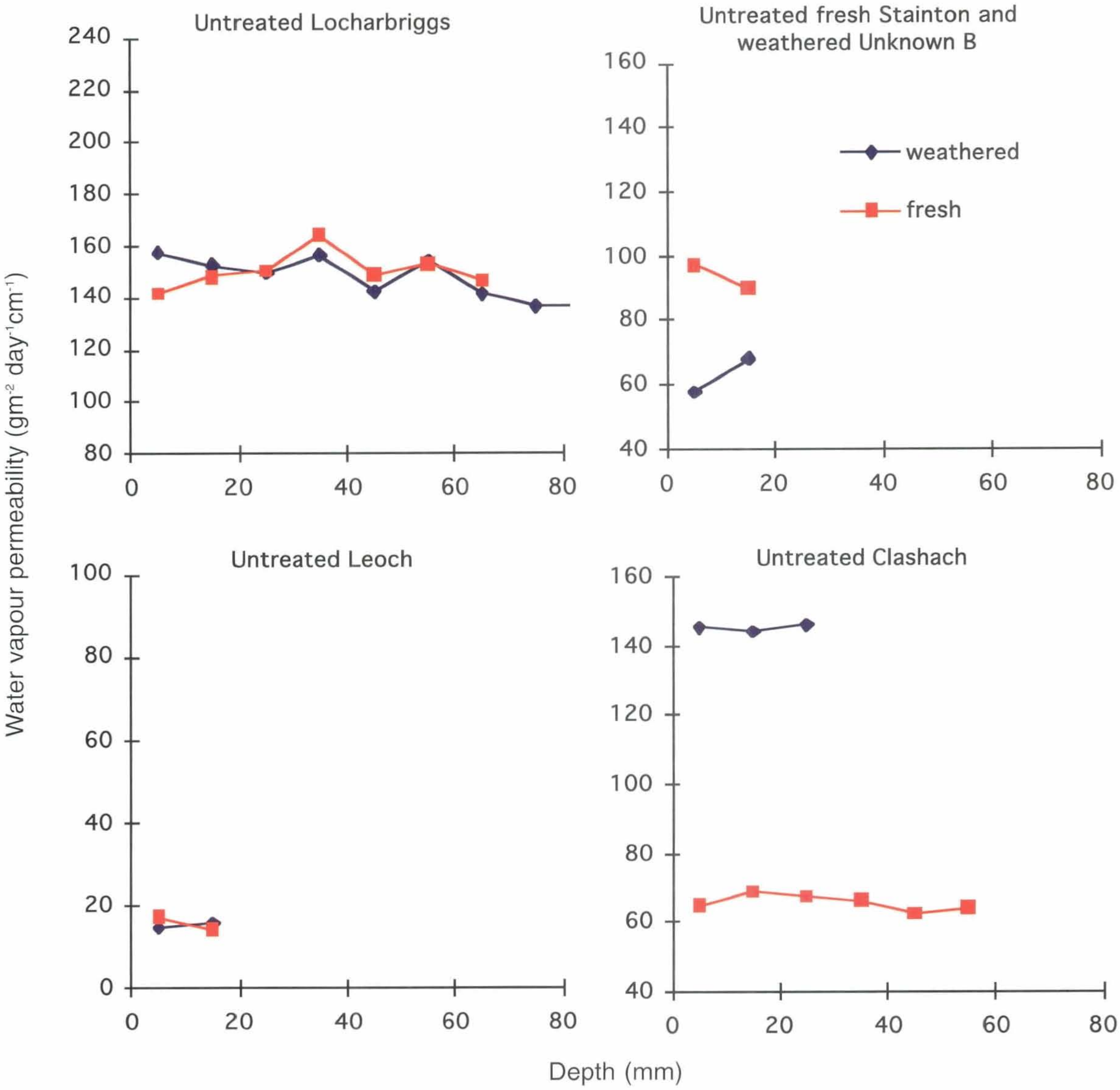


Figure 35a   Water vapour permeability at different depths on a range of sandstones.

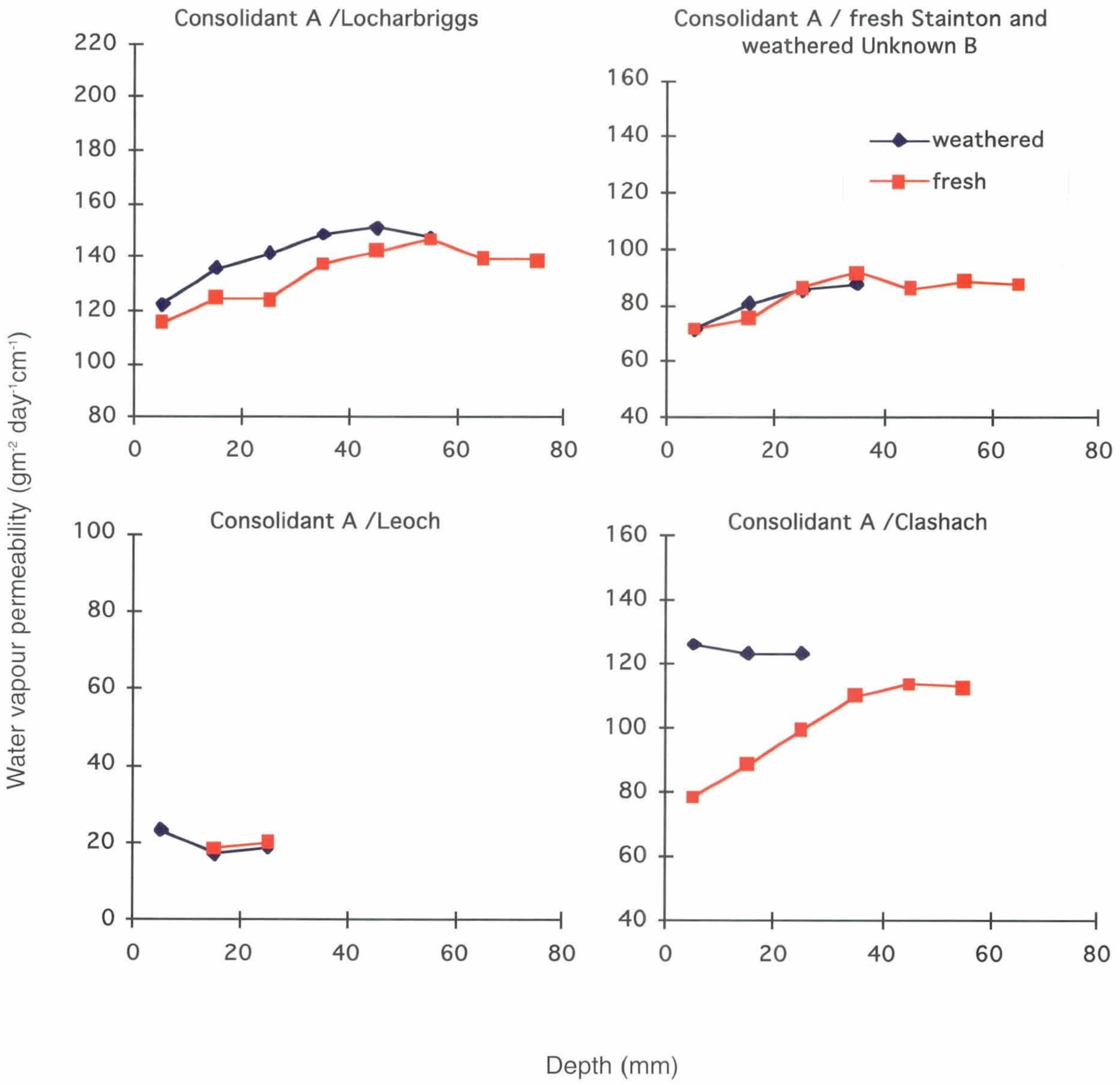


Figure 35b Water vapour permeability at different depths on a range of sandstones treated with Consolidant A.

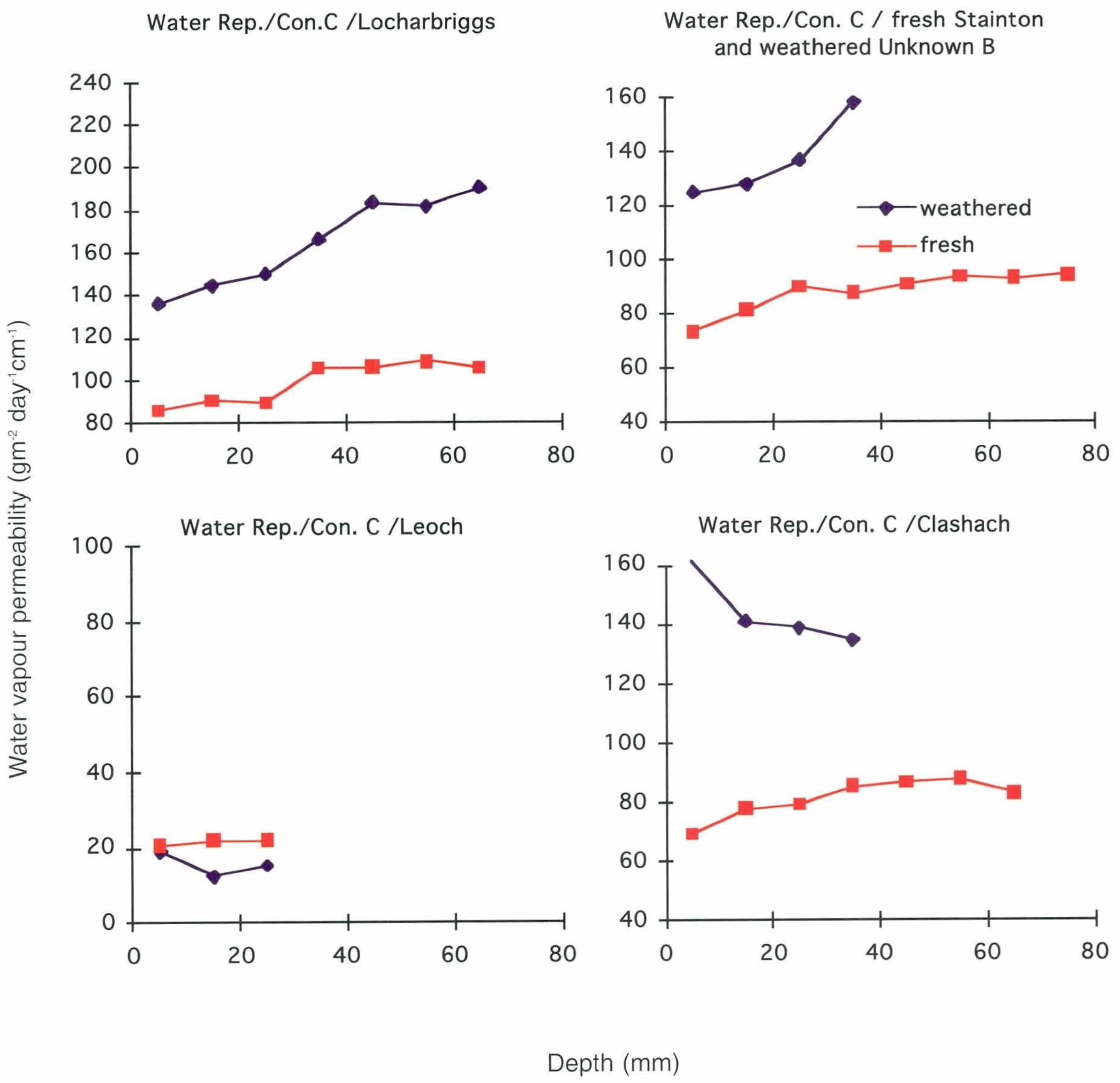


Figure 35c Water vapour permeability at different depths on a range of sandstones treated with Water Rep./Con. C.

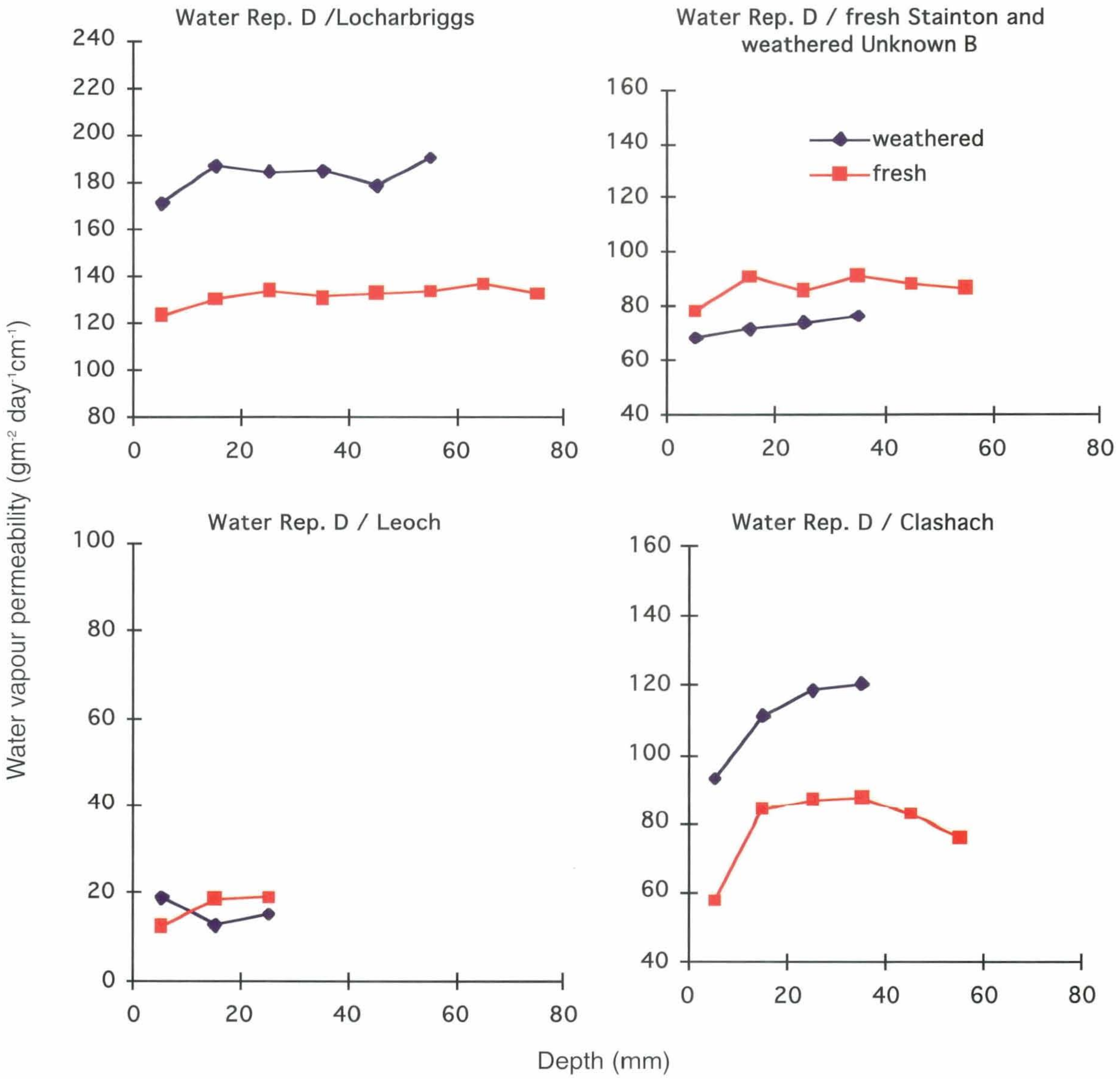


Figure 35d Water vapour permeability at different depths on a range of sandstones treated with Water Repellent D.

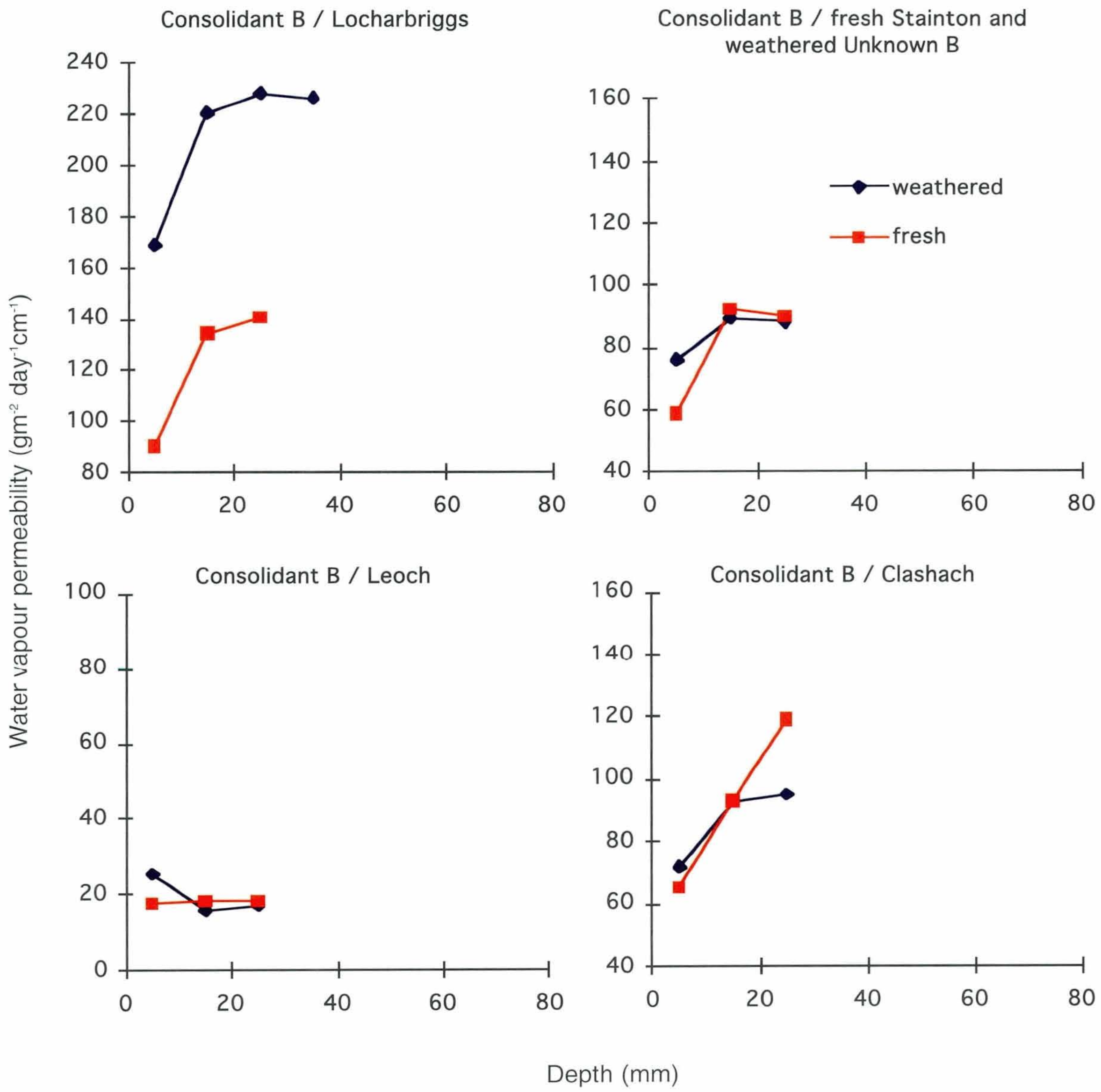


Figure 35e *Water vapour permeability at different depths on a range of sandstones treated with Consolidant B.*

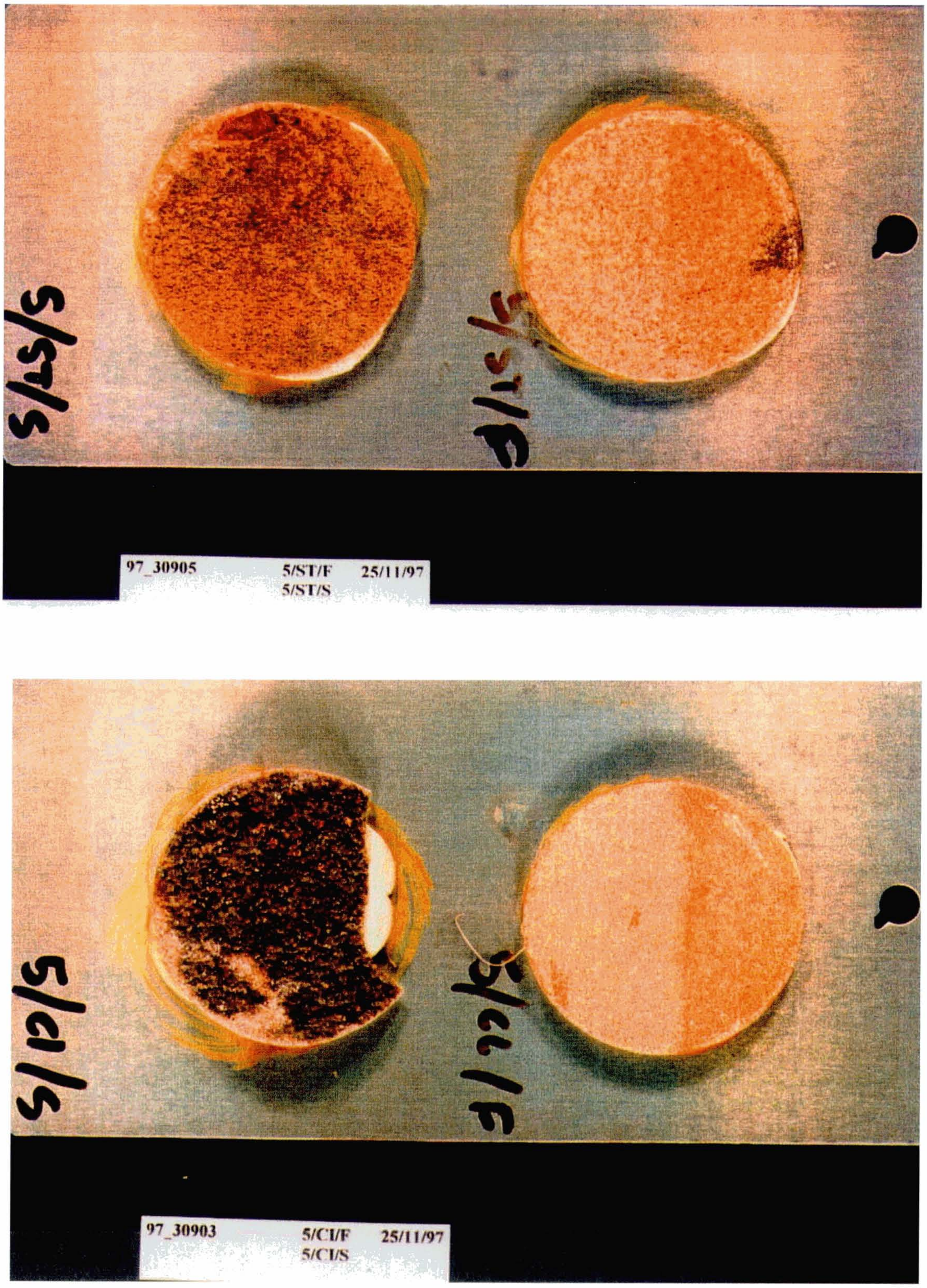


Figure 36a The change in appearance caused by UV-B exposure of Water Rep./Con. C treated samples of: soiled Unknown B (top left), fresh Stainton (top right), soiled Clashach (bottom left) and fresh Clashach (bottom right).

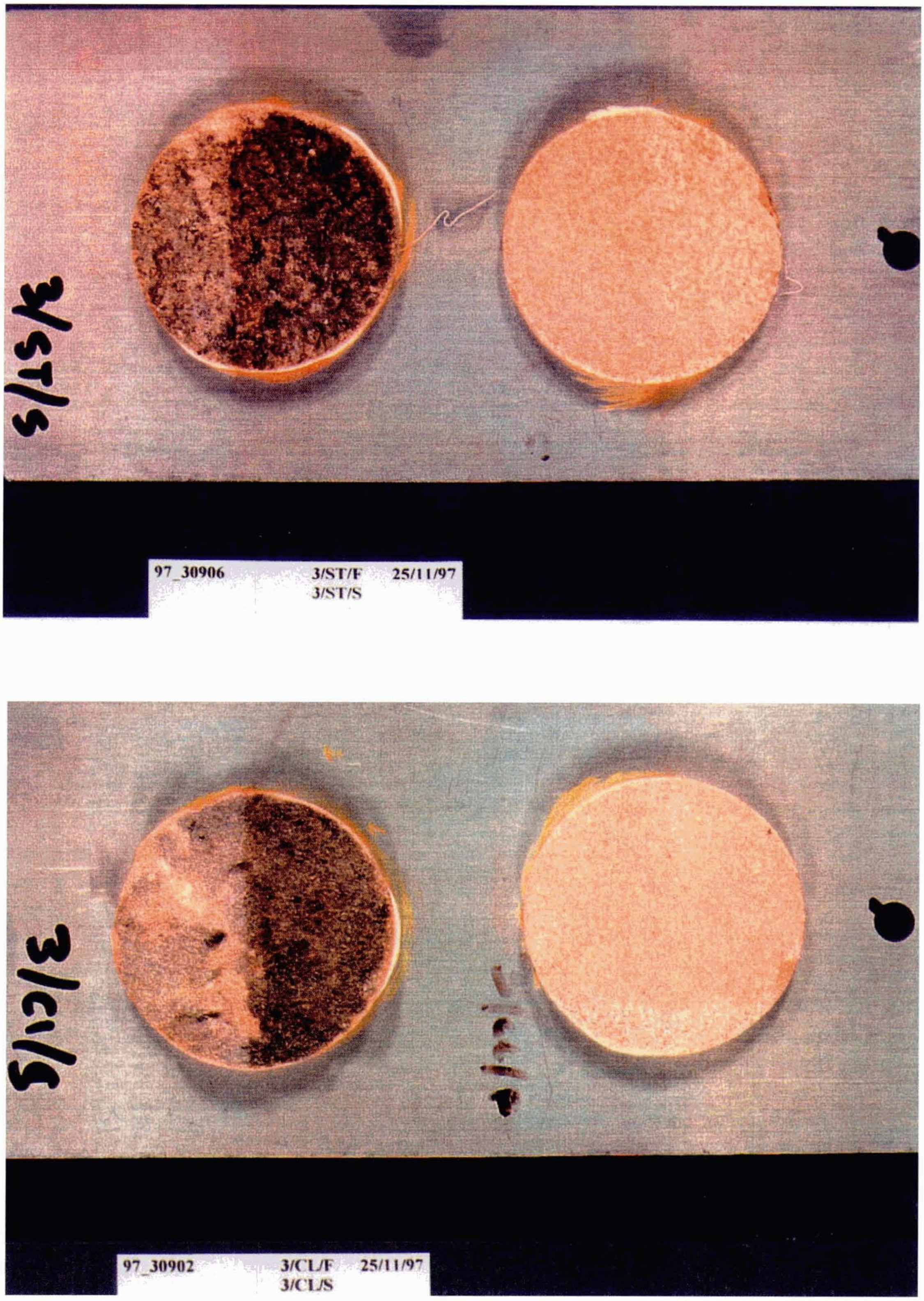


Figure 36b The change in appearance caused by UV-B exposure of Consolidant B treated samples of: soiled Unknown B (top left), fresh Stainton (top right), soiled Clashach (bottom left) and fresh Clashach (bottom right).

Figure 36c The change in appearance caused by UV-B exposure of Consolidant B treated samples of soiled Locharbriggs (left) and fresh Locharbriggs (right).

Exposure to UV-B in this test is not an exact simulation of the type of UV radiation found in daylight. This is because the UV-B comes form an artificial light source, which will produce a different frequency of UV light. Additionally the intensity of the UV radiation in this test is higher than that found in daylight to allow accelerated weathering. The test essentially detects UV sensitivity. If test samples can withstand the conditions of the test, then they are very unlikely to sustain any UV exposure damage. Additionally the Consolidant B and Water Rep./Con. C treated surfaces which have shown UV sensitivity may still not sustain any damage in natural conditions. Real exposure conditions would be required for the best simulation.

Two colour change effects occurred.

(i) **Consolidant B** treated freshly cut surfaces of Locharbriggs, Clashach and Stainton sandstones became lighter in colour due to UV exposure. The original treatment has been shown to darken the surfaces. It may be that the appearance change is a return to the original colour of the stone.

(ii) **Water Rep./Con. C** applied over weathered surfaces of "Unknown B" and Clashach sandstones became substantially lighter, almost bleached; however it is unclear if this is caused by an opaque change in colour of the treatment, or by bleaching of the weathered surface underneath. As no other samples appeared to show bleaching of weathered surfaces, it would appear that a specific effect involving the Water Rep./Con. C has occurred, but it is unclear exactly what. This would require further investigation to determine if the soiled surface is still dark underneath.

4.4.6.2 Freeze thaw tests

To determine if frost cycles will affect treated sandstone freezing and thawing tests were carried out. Cores from the RGU panels of treated Locharbriggs, Clashach, Leoch, Stainton and "Unknown B" sandstones were selected. The range included both weathered and fresh surfaces. The treatments were Consolidant A, Consolidant B, Water Rep./Con. C and Water Repellent D. All cores were subjected to 110 cycles of freezing and thawing. The details of the freeze thaw chamber are noted in Section 3.3.4.2.

During and after the test no frost damage to treated areas was observed on any sample, although untreated parts of the samples did sustain some damage. The treatments therefore do not appear to increase the frost susceptibility of the sandstones.

4.4.7 Dilatometry

The consolidants and water repellents may cause stone masonry to expand or contract. If this occurred over a large areas it could result in cracking and delamination. To assess dimensional changes upon treatment, dilatometry was used. The exact method is detailed in Section 3.3.8.

Cores of Locharbriggs sandstone were laboratory treated with Consolidant A, Consolidant B, Water Rep./Con. C and Water Repellent D. The changes in size between 5 cm wide positioning points was recorded during the application and curing of the treatments. The effects of wetting with water were also assessed. Each core had duplicate positioning studs on either side, giving two results for each situation.

A summary of the largest expansion and contraction changes found due to first treatment and then subsequent effects of water on the cured treatments are listed in Table 11. It should be noted that on some cores the measurements on one side gave different results from other side. This resulted in some cores apparently expanding on one side and contracting on the other. The figures (Figure 37) show all dimensional data when the samples were treated, left to dry and cure for 15 days, and then passed through a wetting cycle.

	On treatment		On water wetting	
	Expansion	**Contraction**	**Expansion**	**Contraction**
Consolidant A	+0.075%	-0.045%	+0.05%	-0.01%
Water Rep./Con. C	+0.11%	-0.0825%	+0.025%	-0.0625%
Water Rep. D	none	-0.045	+0.035%	none
Consolidant B	+0.04%	-0.14%	+0.06%	none
Control	+0.005%	-0.005%	+0.03%	none

Table 11 Maximum and minimum changes in percentage length observed during the tests.

4.4.8 Emissions of volatile organic compounds (VOCs)

4.4.8.1 Total solvent loss

Consolidants and water repellents may emit volatile organic compounds (VOCs) during curing. The concentration, identification and length of time over which they persist could be of importance for health and safety reasons. The VOCs can most easily be observed by recording the weight loss of treated samples of stone using the procedure detailed in Section 3.3.9.1. Note: This test will also detect non-VOC losses such as water vapour from certain chemical reactions.

Samples of Locharbriggs sandstone were treated with Consolidant A, Consolidant B, Water Rep./Con. C and Water Repellent D. The weight increase of the samples was used to determine the weight of treatment. The weight was then measured at suitable times over a period of 1500 hours. The results are shown in Figure 38.

Results showed that for Consolidant A, Consolidant B and Water Rep./Con. C substantial amounts of the treatment evaporated in the first few days until a steady state was reached after 50 hours. This correlates to an initial evaporation rate of 60-100 grams per metre square per day. Water Repellent D treatment had a much slower overall rate of loss. It required over 1000 hours (40 days) until the weight loss appeared to level out.

By weight:

38% of Consolidant A,

12% of Consolidant B,

41% of Water Rep./Con. C, and

22% of Water Repellent D

remained after 1500 hours (60 days). Therefore, it is clear that the majority of the consolidants and water repellents ***as applied*** will be lost by evaporation.

The initial weight losses observed were mostly caused by loss of original solvents used as a transport vehicle and reaction medium. However losses may also include some contribution from the consolidant monomers, partially polymerised monomers, condensation products from reactions (e.g. water, alcohol, acetone, methanol, etc.) or re-evaporation of absorbed atmospheric moisture or chemicals. The loss of consolidant monomer and partially polymerised monomer is likely to be particularly important as this will result in loss of consolidant, which may reduce the level of consolidation.

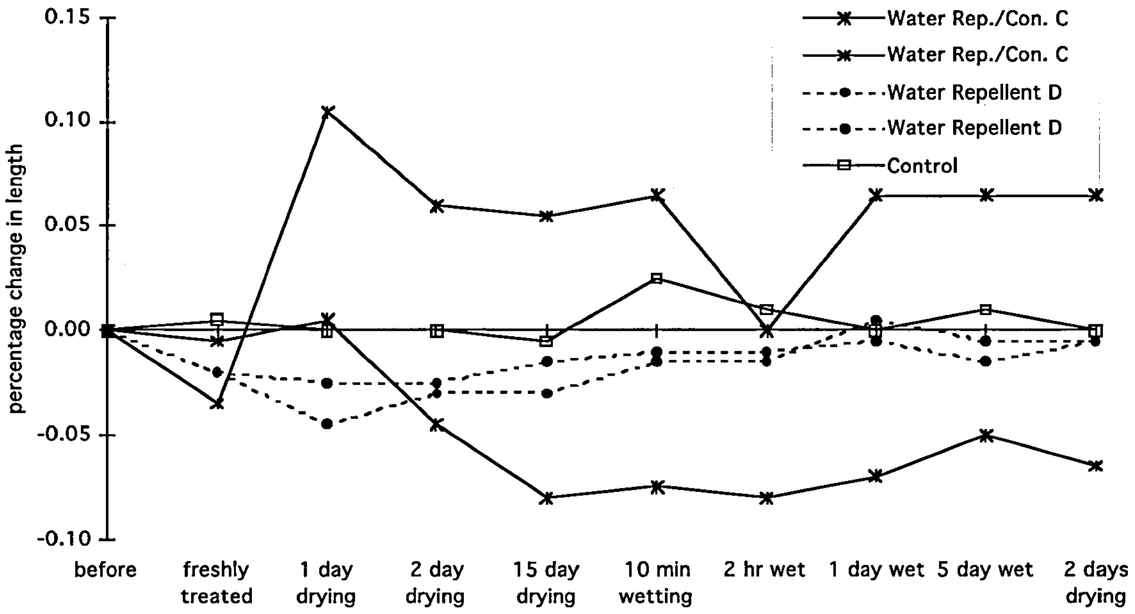


Figure 37a Mean change in Locharbriggs stone dimensions after treatment with Water Repellent D and Water Rep./Con. C. The effects of drying, curing and water wetting are also recorded.

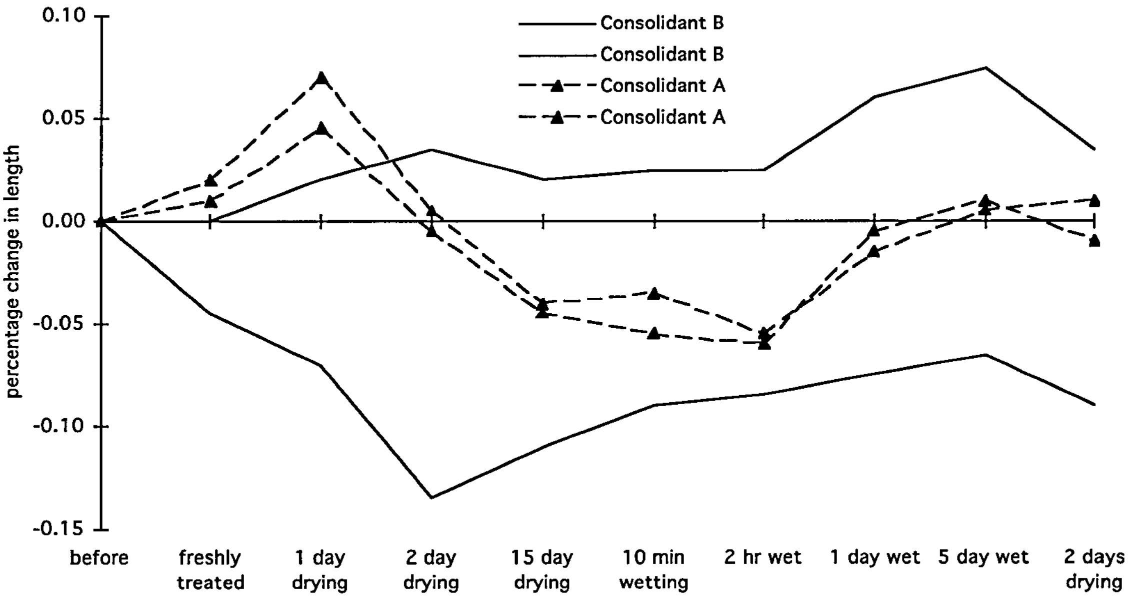


Figure 37b Mean change in Locharbriggs stone dimensions after treatment with Consolidant B and Consolidant A. The effects of drying, curing and water wetting are also recorded.

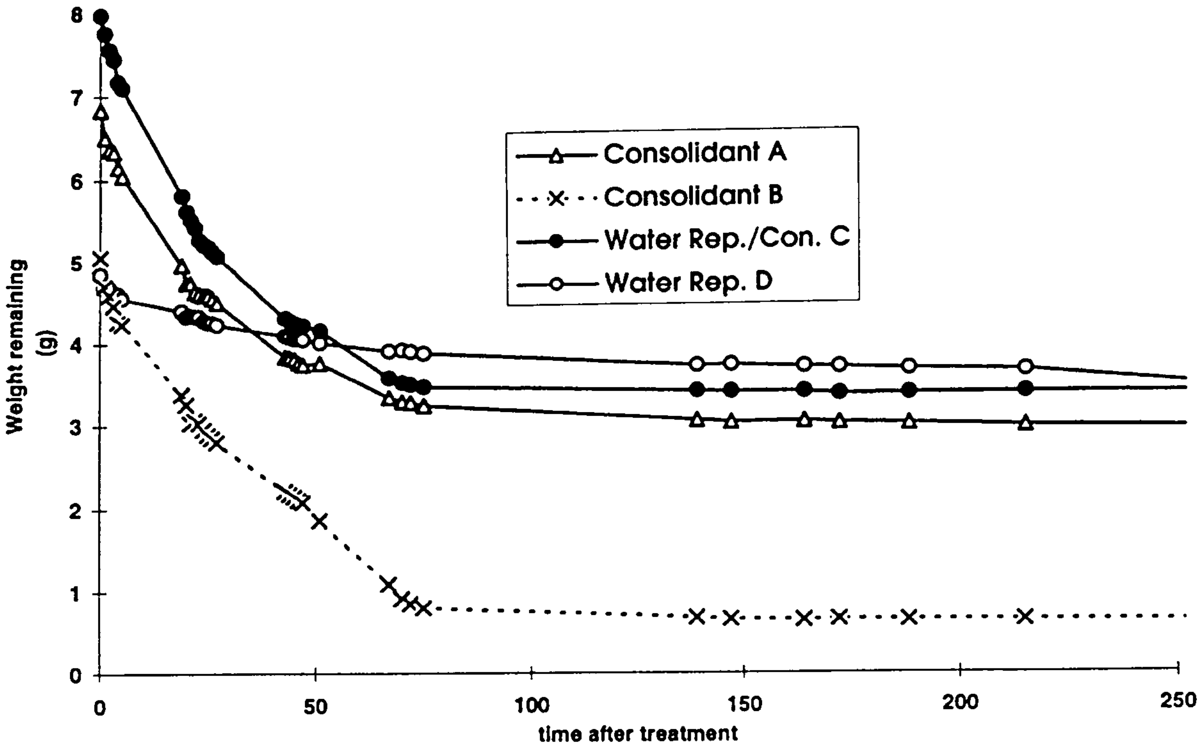


Figure 38a Weight change after treatment and curing over a period of 250 hours.

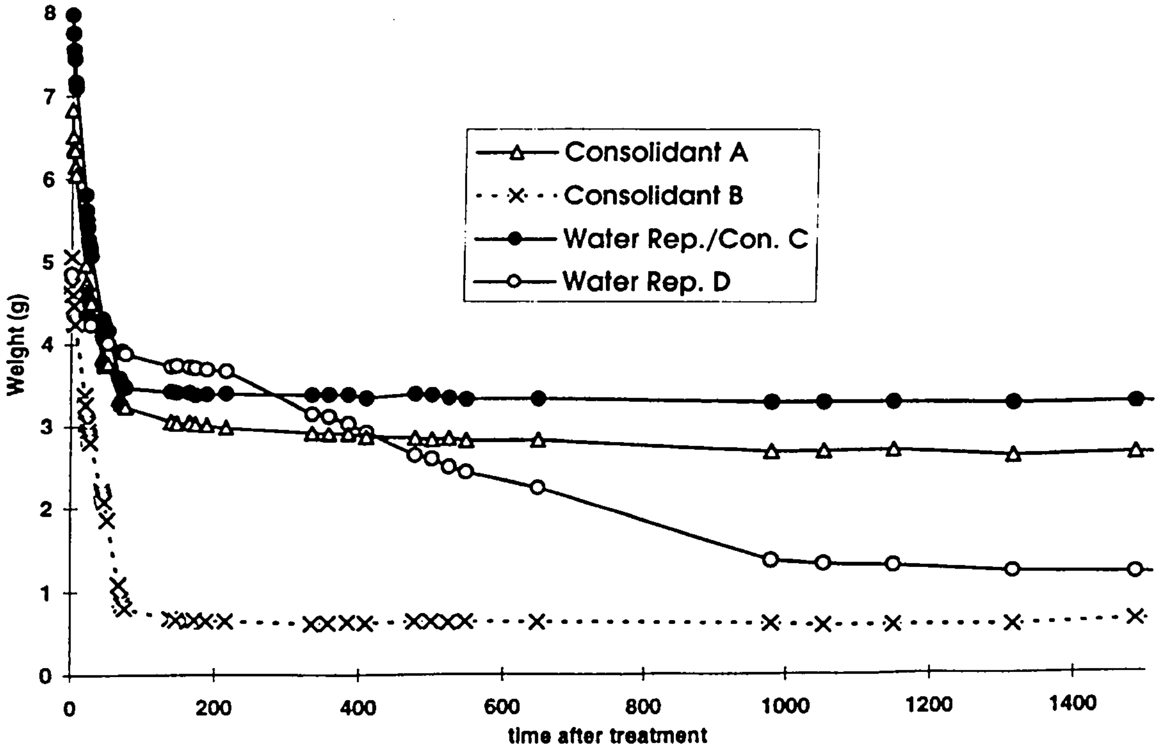


Figure 38b Weight change after treatment and curing over a period of 1500 hours.

4.4.8.2 Identification of volatile organic compounds (VOCs)

The loss of weight found in masonry after treatment is likely to be attributable to the evaporation of VOCs and possibly water. To determine the exact identification of VOCs gas chromatography (GC) with mass spectrometry (MS) was used as detailed in Section 3.3.9.2. Cores of Stainton sandstone were used for the test which were treated with Consolidant A, Consolidant B, Water Rep./Con. C and Water Repellent D. The cores were prepared in foil as detailed previously for weight loss experiments in Section 3.3.9.1. For analysis the samples were placed in a VOC collection chamber. A known flow rate of air through the chamber was used to pass solvents through to a GC and MS apparatus via an intermediary absorption substrate. VOC testing was carried out at 2 hrs and 100 hrs after treatment. The results were interpreted by library search, diagnosis of mass spectrometry data, and cross reference to the weight loss data.

As expected VOCs were found at 2 hrs in all treated samples. At 100 hrs the VOC concentrations had reduced and some VOCs vanished. The main VOCs found are identified in Table 12. Figure 39 shows the individual spectra produced from the GC with each VOC identified. Each VOC detected appears as a spike (peak). Peaks which were identified have the suggested name of the VOC noted. An assessment of the ambient conditions using an untreated core was taken at 24 hrs (Figure 39i).

The weight loss upon dying and curing is shown in Figure 40. The weight losses from cores treated with Consolidant A, Consolidant B and Water Rep./Con. C began to stabilise after 20-100 hrs.

2 hrs	**Alcohol/ acetone**	**Butan-1-ol**	**MEK***	**White spirit**	**Toluene**	**Xylene**	**Silanol**	**Siloxane**
Consolidant A	x		x		x			x
Consolidant B					x			
Water Rep./Con. C	x		x		x	x		x
Water Repellent D	x			x	x		x	
100 hrs								
Consolidant A	x	x	x		x			
Consolidant B					x			
Water Rep./Con. C	x		x		x			
Water Repellent D				x	x		x	

* MEK = methyl ethyl ketone

Table 12 VOCs found by GC and MS after 2 hrs and 100 hrs curing.

The initial weight losses observed were mostly caused by loss of original solvents used as a transport vehicle and reaction medium. However, as pointed out above, there is a range of other sources of volatile compounds. The loss of consolidant monomer and partially polymerised monomer is likely to be particularly important as this will result in loss of consolidant that may reduce the level of consolidation.

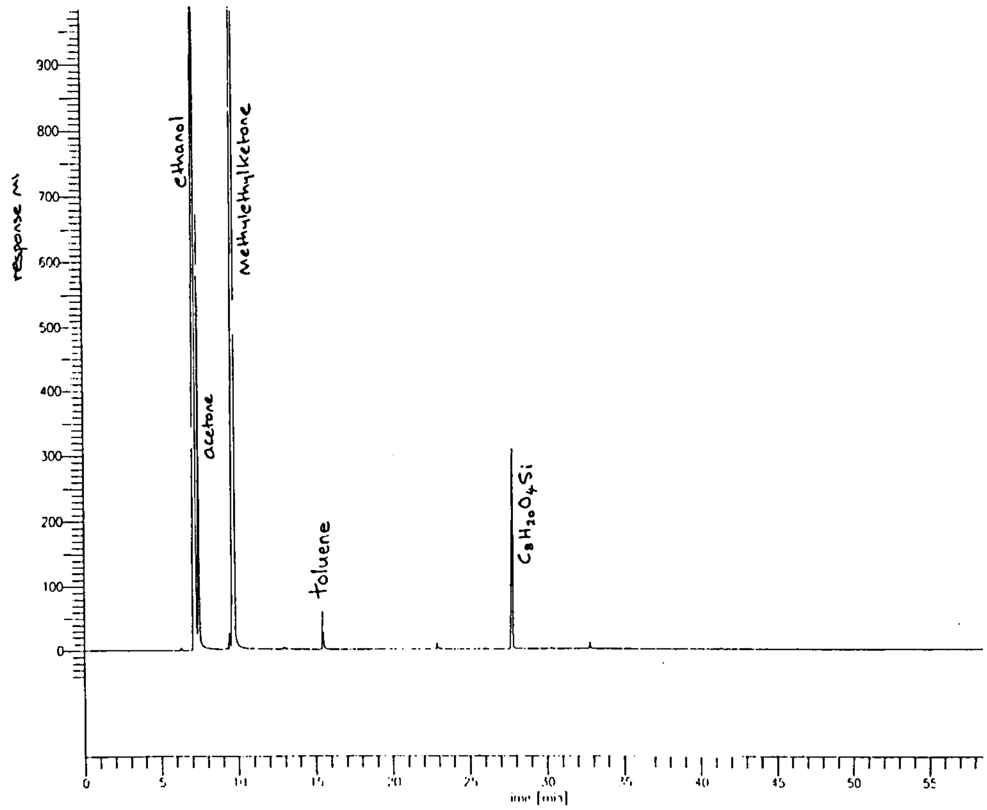


Figure 39a GC spectra of VOCs from Consolidant A treatment after 2 hrs curing.

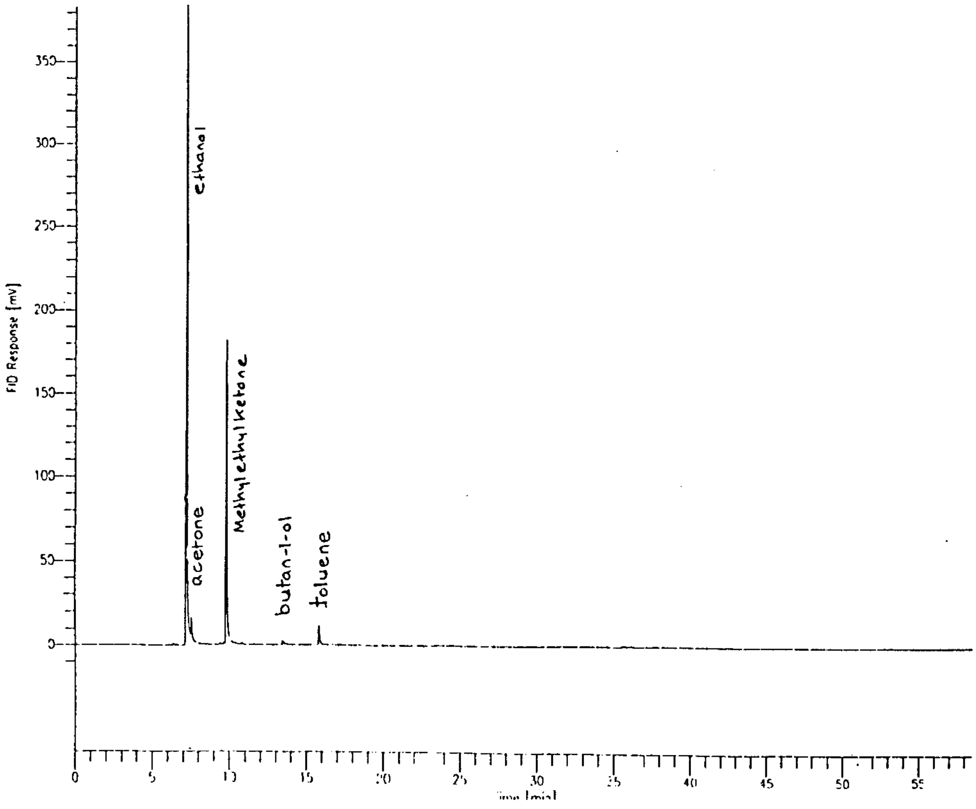


Figure 39b GC spectra of VOCs from Consolidant A treatment after 100 hrs curing.

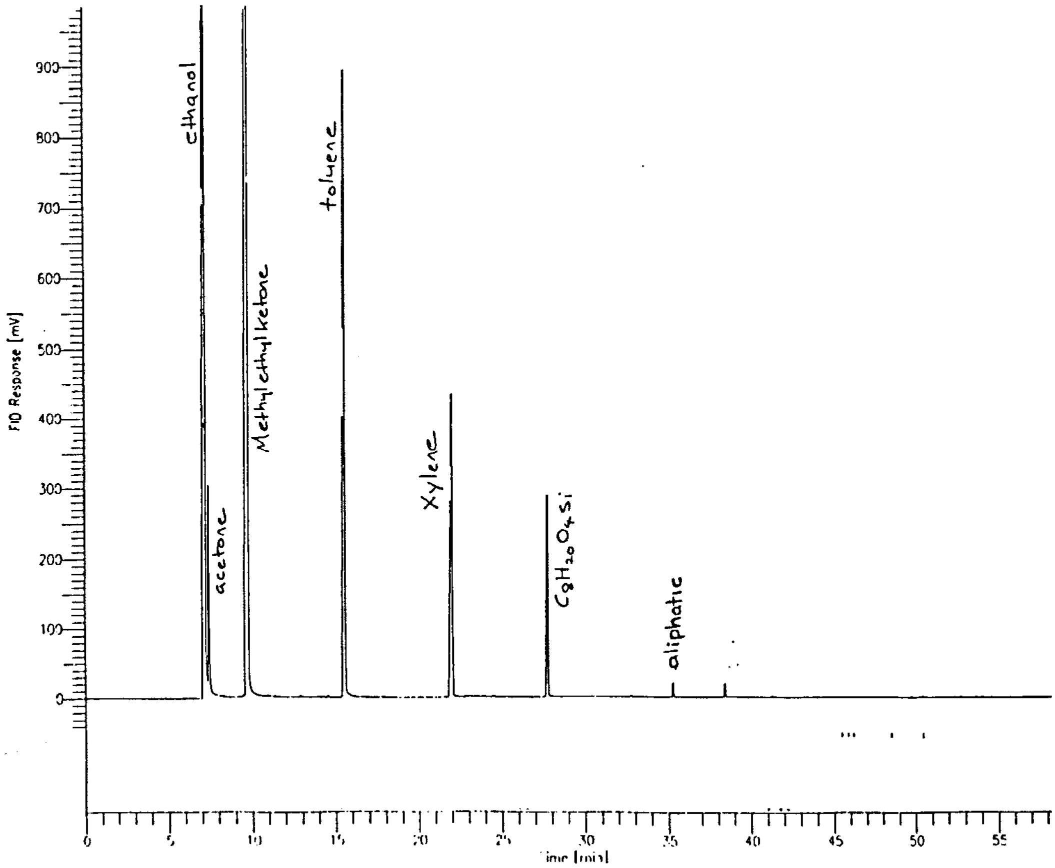


Figure 39c GC spectra of VOCs from Water Rep./Con. C treatment after 2 hrs curing.

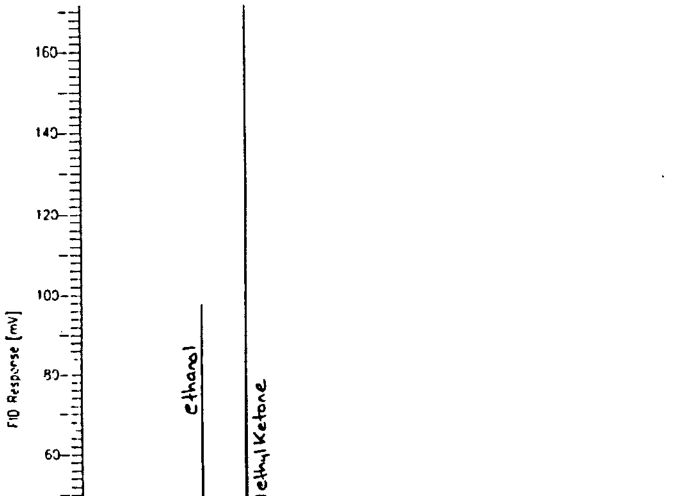


Figure 39d GC spectra of VOCs from Water Rep./Con. C treatment after 100 hrs curing.

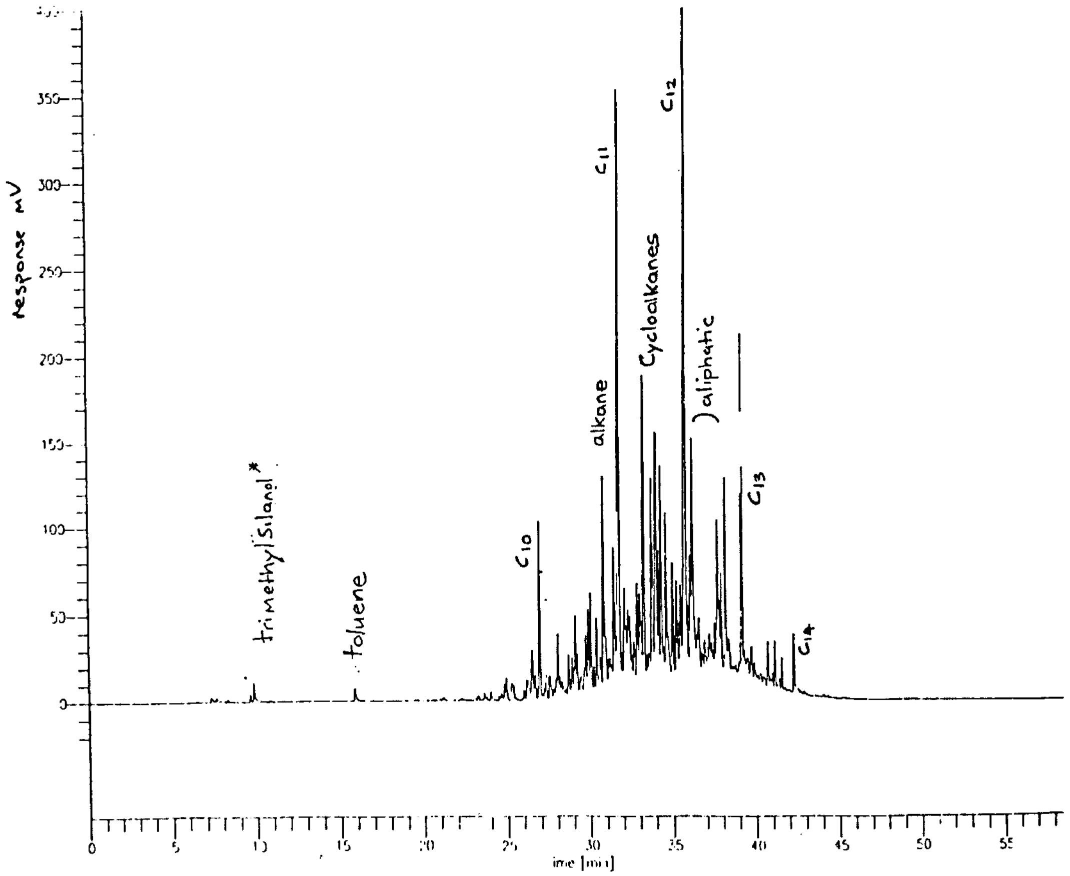


Figure 39e GC spectra of VOCs from Water Repellent D treatment after 2 hrs curing.

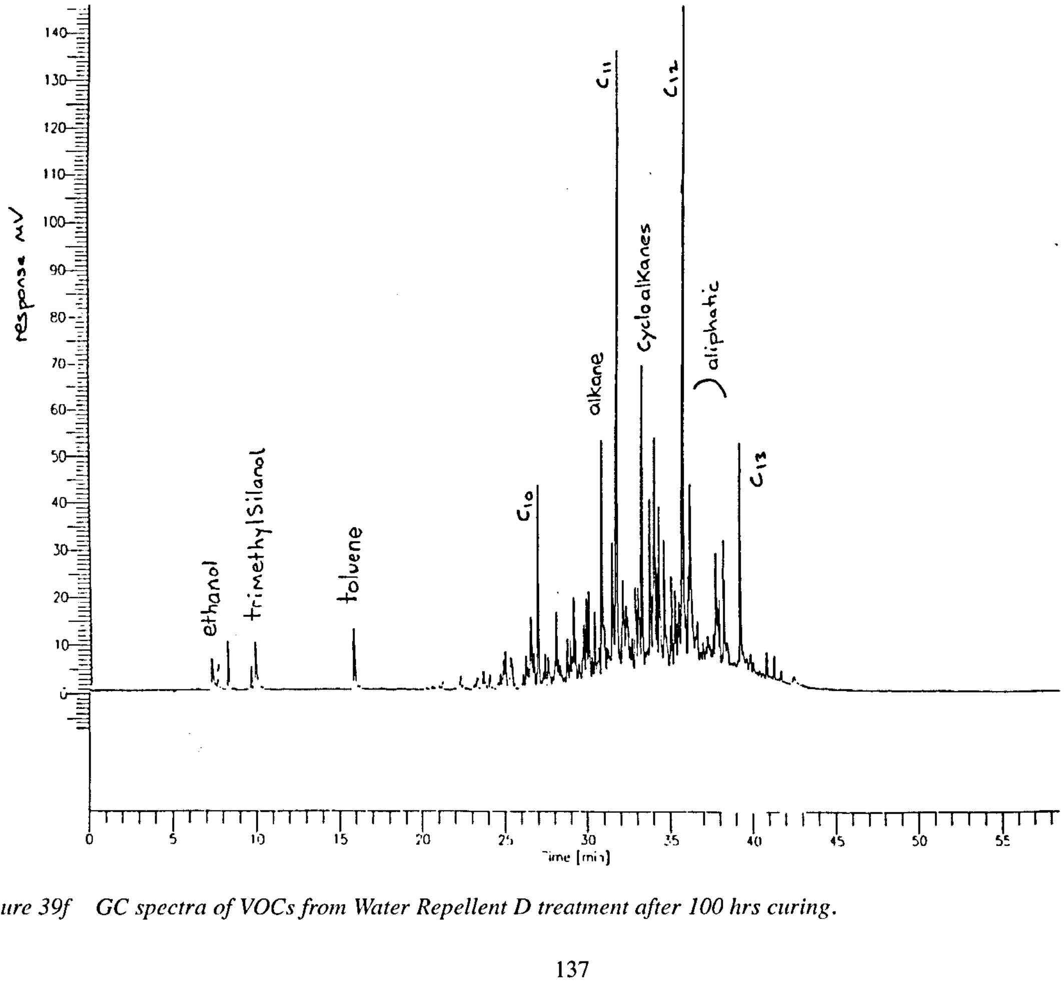


Figure 39f GC spectra of VOCs from Water Repellent D treatment after 100 hrs curing.

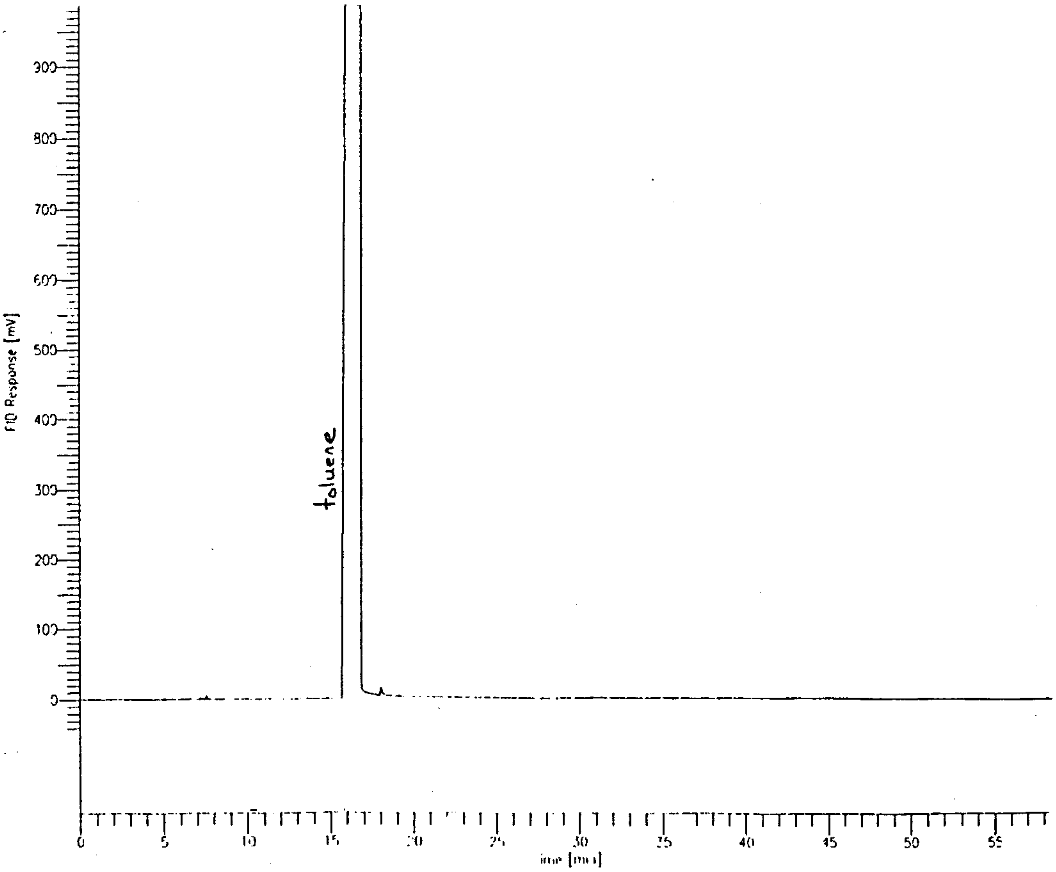


Figure 39g GC spectra of VOCs from Consolidant B treatment after 2 hrs curing.

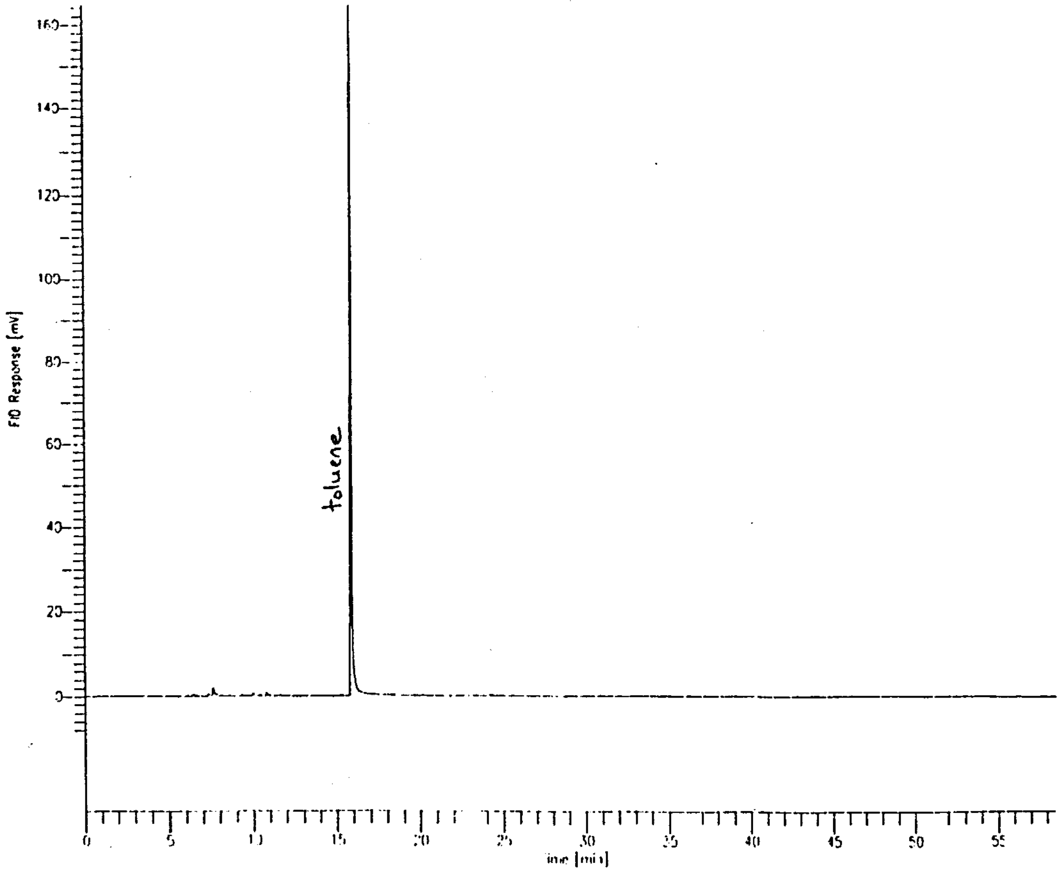


Figure 39h GC spectra of VOCs from Consolidant B treatment after 100 hrs curing.

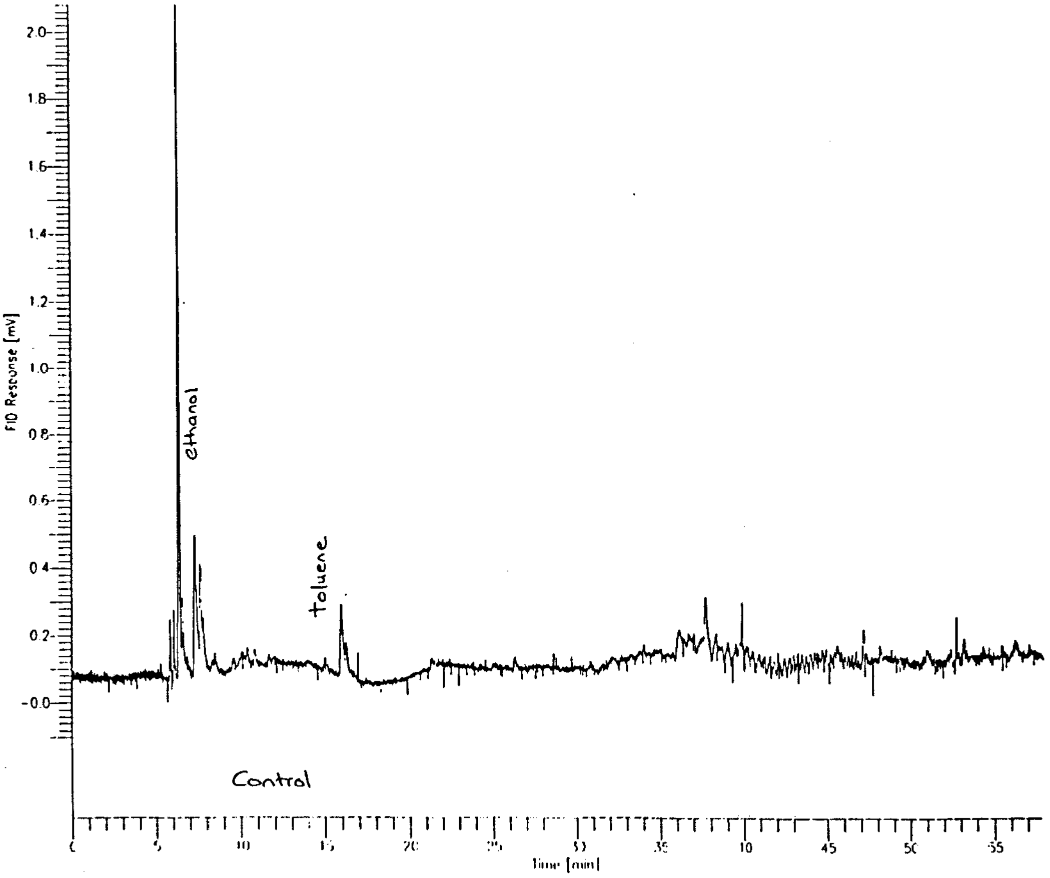


Figure 39i *GC spectra of VOCs from control taken at 24 hrs.*

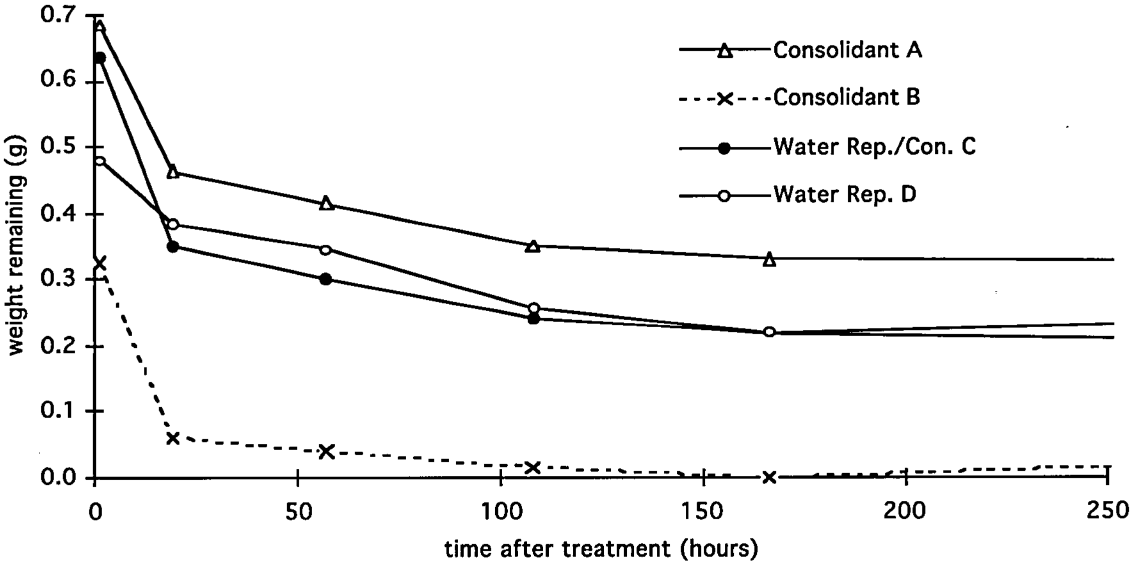


Figure 40 *The weight loss of samples of Stainton sandstone treated with different consolidants and a water repellent.*

Consolidant B

VOCs emitted from Consolidant B were exclusively toluene and no acrylic monomers were observed. This was expected as the treatment was made from solid blocks of Consolidant B, which were dissolved in ten times the weight of pure toluene as a solvent. The acrylic polymer would not be expected to evaporate.

Water Repellent D

Water Repellent D emitted white spirit vapour. White spirit is a mixture of many different VOCs, which can be identified by its characteristic broad GC spectra comprising many peaks rather than by individual components. Fully comprehensive VOC identification for white spirit is difficult as any other additional compounds can be hidden in the spectra. However, the main white spirit peaks were characterised using mass spectroscopy. No additional compounds were identified in this region which could not have been present in white spirit itself, although it is possible that smaller traces of VOCs which are unknown are clouded by the "white spirit" signal. Observation of other areas of the spectra detected small amounts of compound which may be a silanol (organo-silica based), although it was difficult to identify its exact nature. This would be a component of the consolidant rather than the solvent and so implies that some of the added water repellent evaporates away before setting.

Consolidant A and Water Rep./Con. C

Consolidant A and Water Rep./Con. C produced spectra which showed several VOCs. There were VOCs which appear to come purely from the solvent such as toluene which was emitted from Water Rep./Con. C and Consolidant A. Alcohol and acetone were present which may have come from either the solvent or the reaction products from polymerisation of the consolidant.

A siloxane (organo-silica based) was present after two hours, but was not observed after 100 hours. This would be a component of the consolidant rather than the solvent. The organo-silica based compounds which were produced from Consolidant A, Water Rep./Con. C and Water Repellent D are difficult to exactly identify. This is because there are a range of molecular structures possible for the formula suggested in the GC:MS analysis. However substantial loss of consolidant monomer or polymer would reduce the effect of consolidation.

4.4.8.3 Comparison of VOC emissions from mortar and sandstone

Samples of three mortars, one lime mortar (2:5 lime:sand) and two cement mortars (1:1:6 and 1:3:12 cement:lime:sand), and Locharbriggs sandstone were treated with solvents (white spirit and toluene), Consolidant B, Water Rep./Con. C and Water Repellent D. The rate of evaporation from the samples was measured. The methodology is given in Section 3.3.9.3.

Graphs in Figure 41 show the weight loss from treated prisms (mean of three replicates) during the evaporation process following treatment, displayed as percentage treatment retained, the initial weight of the treated sample being taken as 100%. As the graphs show a continuous curve which trends towards a final horizontal line as the sample weight approaches stability, it is not easy to determine the precise time at which the sample achieved a stable weight (i.e. the time at which solvent evaporation was complete. In the data used here, the time at which evaporation was complete has been taken to be the time at which, within four successive measurements of sample weight, two measurements showed slight weight gain (since when a sample reaches "constant" weight slight increases and decreases in weight may be measured due to changes in humidity or errors in measurement).

For some samples, continuing weight gains were measured after evaporation of solvents was complete. This was found to be the case for lime and some 1:1:6 mortar samples. In both cases the weight gains over time are assumed to be due to carbonation of the mortar. The samples were cut from mortar cubes a few days before use, and testing with phenolphthalein (Section 4.5.2) has shown that carbonation was incomplete for most cubes. It has been possible to correct the data for carbonation using weight gains measured from the samples treated with toluene and white spirit since the percentage treatment retained after solvent evaporation from these samples should be zero. Any weight gains measured in these samples can therefore be assumed to be due to CO_2 absorption due to carbonation and by subtracting this value from the remaining samples the data can be corrected for errors introduced by carbonation.

The time taken for the samples to achieve constant weight is shown in Table 13. Of the materials tested toluene and toluene-based Consolidant B were the fastest treatments to achieve constant weight. The solvent alone took about 150-200 hours (about 6-8 days) for solvent loss to be fairly complete. Where the solvent was used as a carrier for Consolidant B solvent evaporation was slower (200-500 hours, 8 to 20 days), presumably due to both porosity reduction in the treated samples and perhaps because the consolidant itself retained the solvent for longer. For Water Rep./Con. C treated samples solvent evaporation for fairly complete by 500-600 hours (20-24 days). The solvent in this treatment is a mixture of butanone (methyl ethyl ketone) and toluene (Table 2). Water Repellent D uses white spirit as a solvent. The Water Repellent D and white spirit treated samples took the longest time to achieve constant weight: white spirit took about 600-2200 hours (25-92 days), Water Repellent D took about 1100-4400 hours (46-183 days).

Although there were some inconsistencies in the results shown in Table 13, generally solvent evaporation was fastest from Locharbriggs sandstone and next fastest from 1:3:12 or 1:1:6 mortar. Lime mortar had the slowest evaporation rates. These results suggest that evaporation was generally faster from less porous materials. These effects of porosity on drying rates were more pronounced for treatments where the drying period was relatively long (i.e. Water Rep. D & white spirit). It might be expected that substrates with a higher porosity would dry more quickly, however, the slower drying rates measured here for more porous substrates appear to be caused by greater initial uptake of treatments in the more porous materials (Table 14).

	Time to achieve constant weight (hours)				
Substrate (% porosity)	**Con. B**	**Water Rep/Con.C**	**Water Rep. D**	**Toluene**	**White spirit**
Lime mortar (32.6)	478	502	4443	199	2206
1:3:12 mortar (31.3)	239	501	2374	148	2063
1:1:6 mortar (27.2)	478	501	2115	215	2064
Locharbriggs sst (22.2)	194	621	1149	151	621

Table 13 Mean time (hours) for samples to achieve constant weight.

	Amount of treatment initially taken up (g/cc x 100)				
Substrate	**Con. B**	**Water Rep/Con.C**	**Water Rep. D**	**Toluene**	**White spirit**
Lime mortar	15.8	29.0	18.6	30.5	20.5
1:3:12 mortar	11.5	14.2	10.7	18.0	15.0
1:1:6 mortar	4.2	7.6	3.5	9.7	6.5
Locharbriggs sandstone	9.5	12.9	9.6	10.0	7.0

Table 14 Amount of treatment initially taken up by samples.

The amounts of treatment retained by the samples are shown in Figure 41 and Table 15. As would be expected, the amount of solvent (toluene and white spirit) retained was close to zero. For Consolidant B the amount of consolidant retained was approximately 10%. Since this consolidant was made up as 10%w/v in toluene the percentage retained was in all cases close to the value which would have been predicted. For Water Rep./Con. C there was some variation in the results. Most was retained in the Locharbriggs sandstone sample. It is possible that this reflects lower losses of the silane monomer from the sandstone where polymerisation and bonding to the siliceous minerals in the sandstone may be more rapid. Polymerisation is inhibited in calcareous substrates (Section 2) and this allows more of the monomer to evaporate before it has time to polymerise and be retained in the substrate. The amount of treatment retained in 1:1:6 mortar samples may be low because the amount of treatment taken up by the samples was low (Table 14) and consequently the treatment did not penetrate deeply into the mortar allowing more unpolymerised material to evaporate before polymerisation could occur. The amount of Water Repellent D retained was relatively low in all substrates but was again higher in Locharbriggs sandstone.

	Treatment retained after solvent evaporation (%)				
Substrate	**Con. B**	**Water Rep/Con.C**	**Water Rep. D**	**Toluene**	**White spirit**
Lime mortar	9.9	35.0	3.6	0	0
1:3:12 mortar	9.8	37.4	5.4	0	0
1:1:6 mortar	7.5	32.4	3.4	0	0
Locharbriggs sandstone	10.3	40.3	7.5	0	0.4

Table 15 Percentage treatment retained by samples.

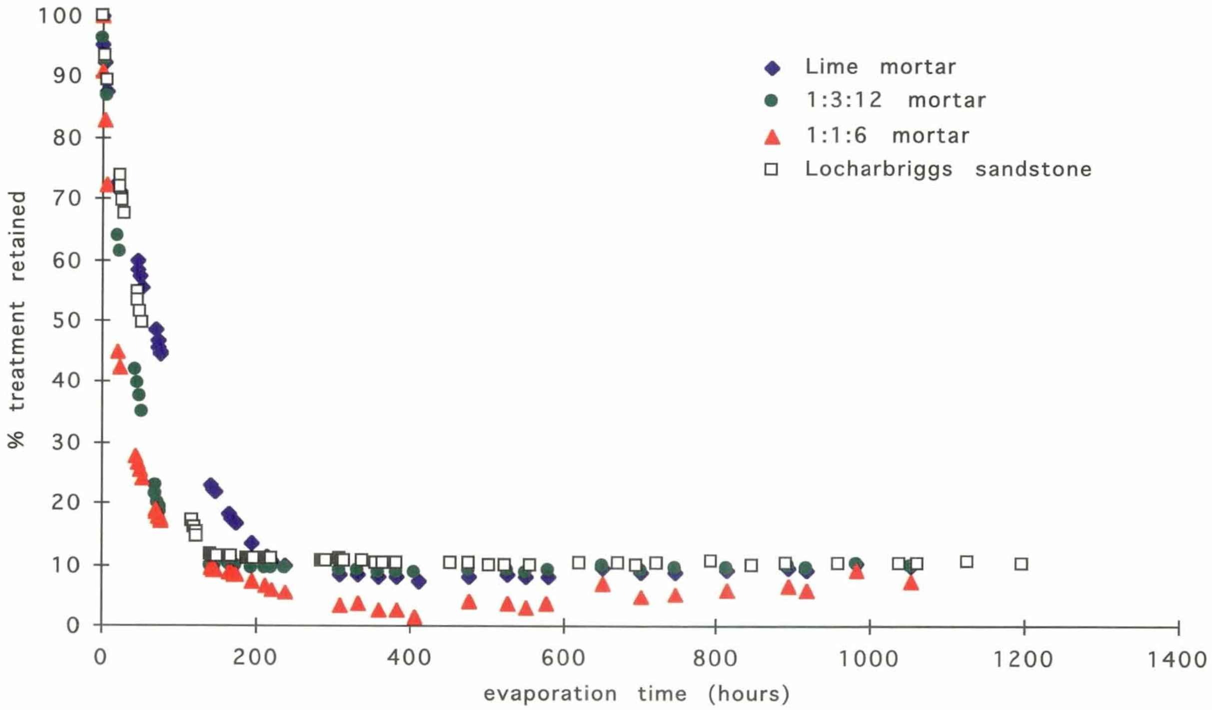


Figure 41a Percentage Consolidant B retained in samples during evaporation process following treatment.

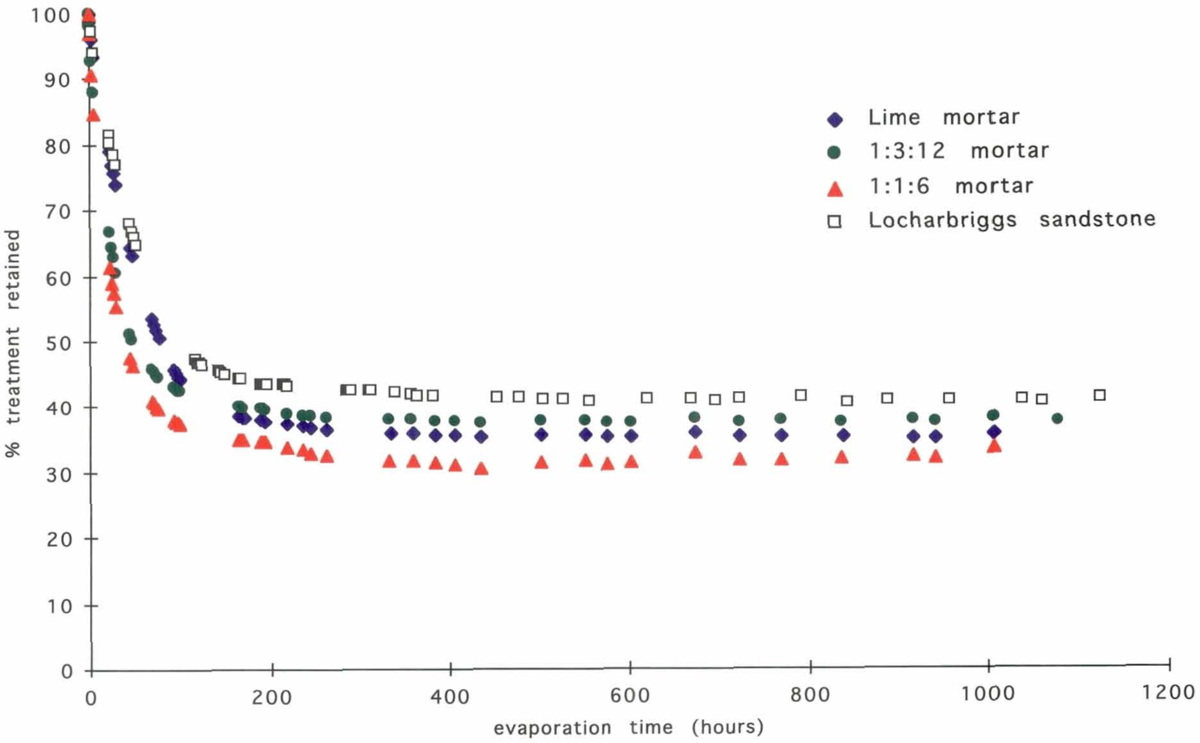


Figure 41b Percentage Water Rep./Con. C retained in samples during evaporation process following treatment.

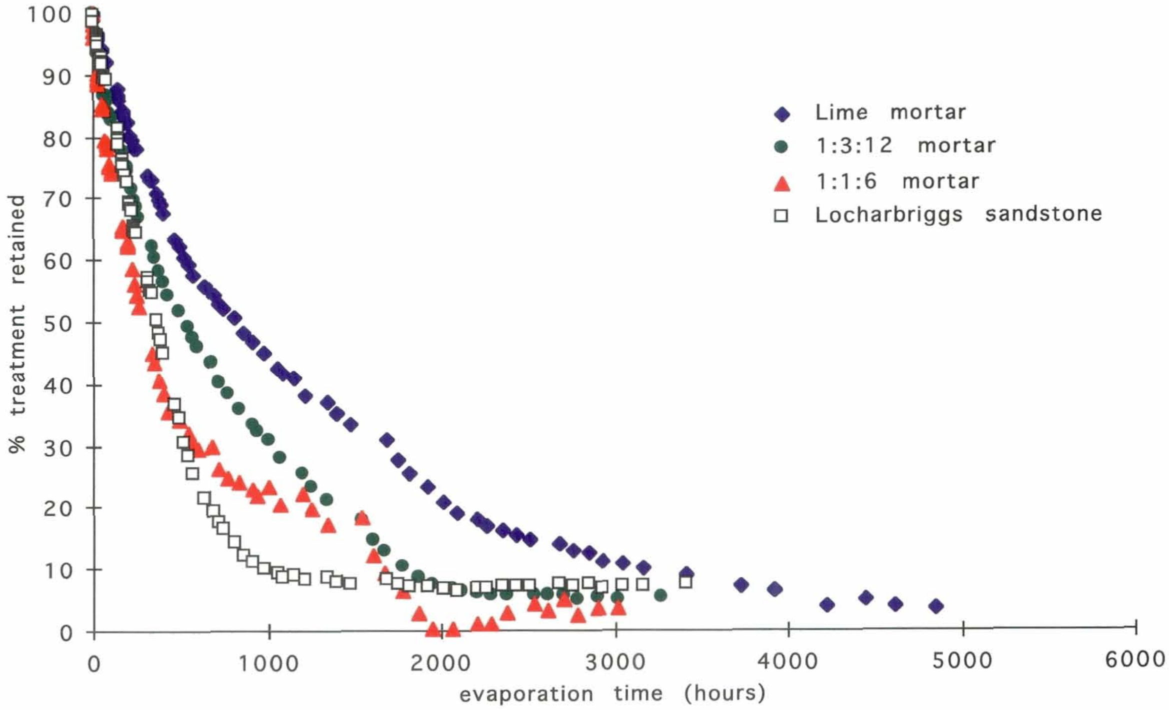


Figure 41c Percentage Water Repellent D retained in samples during evaporation process following treatment.

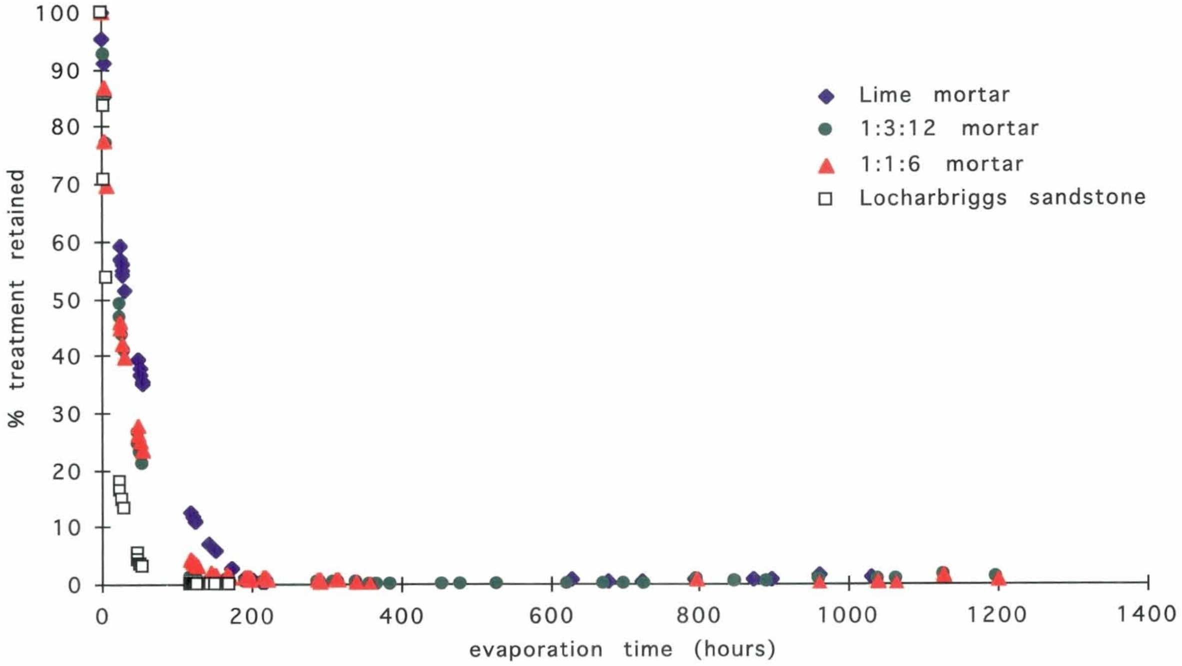


Figure 41d Percentage toluene retained in samples during evaporation process following treatment.

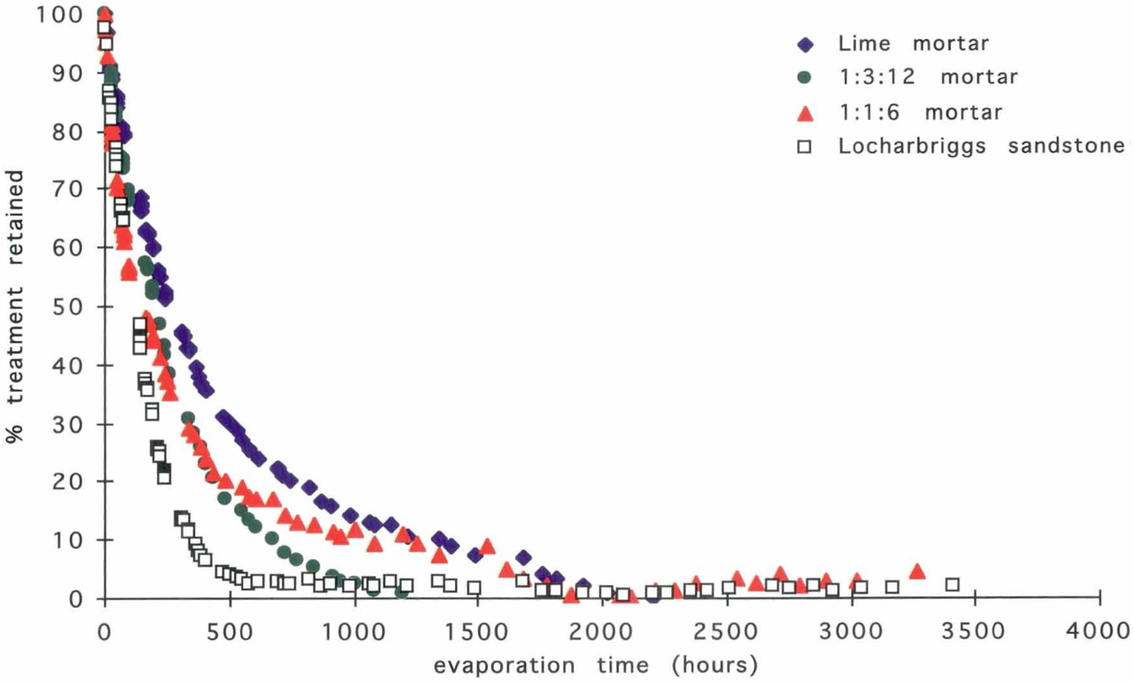


Figure 41e Percentage white spirit retained in samples during evaporation process following treatment.

4.4.9 Scanning electron microscope results

Using scanning electron microscopy to examine the treated samples for residues of consolidant and water repellent treatments was not found to be a useful method for locating the treatments or for determining the depth of penetration of treatments. In practice, the amount of material deposited in sandstone under the conditions used here was very small and difficult to identify by SEM.

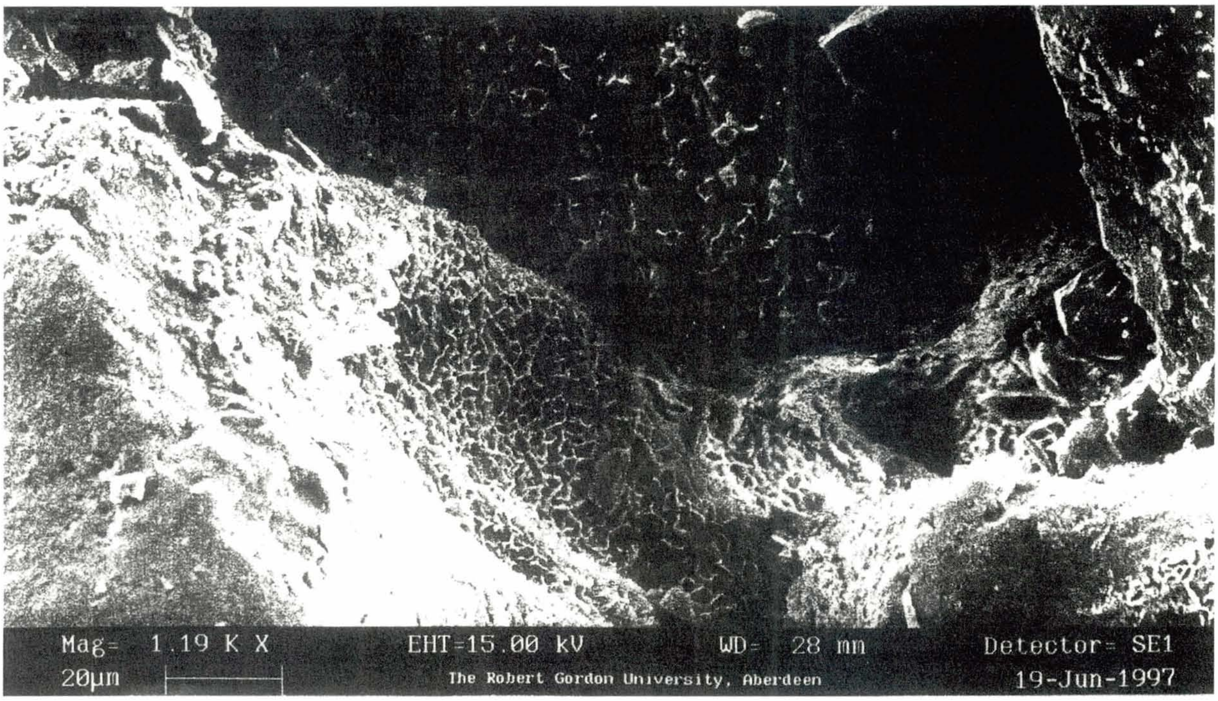


Figure 42a (Water Repellent/Consolidant C) Scanning electron microscopy image of treated, fresh Locharbriggs sandstone showing material which might be taken for consolidant- flaky, superficial deposits. However, inspection of untreated Locharbriggs sandstone (below) shows similar material which is likely to be smectite clay.

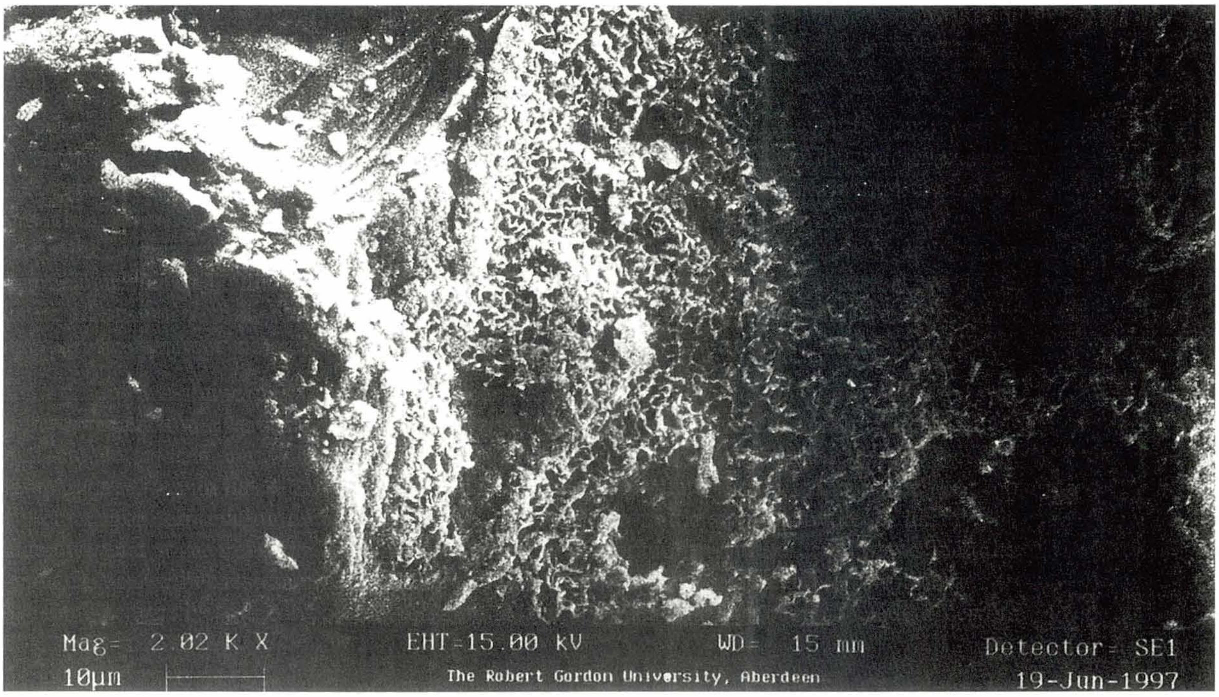


Figure 42b (Water Repellent/Consolidant C) Scanning electron microscopy image of untreated, fresh Locharbriggs sandstone showing deposits of flaky, superficial material assumed to be smectite clay, not consolidant.

4.4.10 Mercury porosimetry of test panel sandstones

Measurements of total porosity (Table 16) by mercury porosimetry can show whether treated/untreated or external/internal samples from sandstones differ. For instance, if a treatment (or soiling) had filled the pore space on the outside of a treated sandstone, then we should see a substantial reduction in total porosity compared to the interior of the sample. More subtle changes in pore size are shown by graphs of pore size distribution (Figure 43). For instance, if the main pores had become lined with a consolidant, then this might show up as a reduction in the modal pore size distribution (i.e. the dominant pore size), since lining of pores should reduce their internal dimensions. If larger pores become filled with a mesh of polymers then this might result in a loss of larger pores, but an increase in the number of smaller pores.

The data in Table 16 show the total porosity of the sandstones (i.e. the total void space in the stone) but give no information on the pore sizes. The samples are shown in pairs of soiled and fresh sandstone (Stainton fresh is paired with Unknown B soiled). Figure 43 shows some examples of pore size distribution (PSD) measurements in the samples. These graphs show the pore size (diameter in microns) along the horizontal axis and the incremental volume of mercury intruded on the vertical axis. Since pore size is measured by intrusion of mercury into the sample, peaks in this graph indicate the pore sizes in the stone. The graph in Figure 43 therefore indicates that most of the pores in this sandstone were about 10 (m in diameter. Due to the large number of samples, only a selection of results can be shown graphically therefore information on changes observed in pore size distribution have been summarised in Table 17.

Panel	**1**		**2**		**5**		**3**		**4**	
Treatment	**Controls**		**Con. A**		**Con. B**		**Water Rep./Con. C**		**Water Rep. D**	
Sample type	**Ext**	**Int**	**Ext**	**Int**	**Ext**	**Int**	**Ext**	**Int**	**Ext**	**Int**
Stone type										
Clashach fresh	15.4	16.0	15.3	17.3	16.3	18.8	17.0	17.8	17.9	16.8
Clashach soiled	22.4	23.7	22.0	25.2	20.0	24.1	22.2	25.4	21.8	22.8
Leoch fresh	7.7	7.7	7.2	7.0	8.5	7.2	7.2	7.2	9.4	7.9
Leoch soiled	8.3	8.1	8.1	6.4	7.1	6.5	11.7	9.8	8.7	7.4
Locharbriggs fresh	24.1	24.4	23.1	25.2	19.7	20.9	18.6	18.2	21.6	20.4
Locharbriggs soiled	24.7	24.8	22.2	25.3	26.7	27.0	25.1	24.2	19.2	24.8
Stainton fresh	18.8	17.6	14.4	17.5	17.0	18.2	18.4	17.8	17.4	17.9
Unknown B soiled	16.9	17.2	15.8	19.6	19.8	19.0	18.9	20.8	16.9	16.1
Mean (exclude Leoch)	**20.4**	**20.6**	**18.8**	**21.7**	**19.9**	**21.3**	**20.0**	**20.7**	**19.1**	**19.8**
Difference (Ext-Int)	**-0.2%**		**-2.9%**		**-1.4%**		**-0.6%**		**-0.7%**	

Ext: external surface sample

Int: internal sample (beyond treatment penetration)

Table 16 Results of mercury porosimetry of sandstone samples from test panels. Showing total effective porosity (%) for samples from the exterior and interior of sandstones. Exterior samples are taken from consolidant or water repellent treated sandstone, interior samples are from beyond the maximum depth of penetration of the treatments.

Treatment	Sandstone	Soiled or fresh	Mode of PSD of treated sandstone (μm)	Mode of PSD of untreated sandstone (μm)	Is pore diameter reduced on treated sandstone?
None	Locharbriggs	F	14.80	18.86	yes
	Locharbriggs	S	20.4	521.98	yes
	Clashach	F	15.56	15.56	no
	Clashach	S	27.5	129.76	yes
	Stainton	F	7.98	7.98	no
	Unknown B	S	1.79	2.12	yes
	Leoch	F	0.0403	0.0384	no
	Leoch	S	0.0686	0.0726	yes
Consolidant A	Locharbriggs	F	16.25	18.68	yes
	Locharbriggs	S	15.94	15.94	no
	Clashach	F	19.90	23.93	yes
	Clashach	S	25.76	29.85	yes
	Stainton	F	7.35	8.60	yes
	Unknown B	S	2.87	3.35	yes
	Leoch	F	0.0556	0.0474	no
	Leoch	S	0.0109	0.0404	yes
Consolidant B	Locharbriggs	F	25.22	30.53	yes
	Locharbriggs	S	22.13	25.06	yes
	Clashach	F	25.72	18.90	no
	Clashach	S	16.12	22.06	yes
	Stainton	F	7.36	7.36	no
	Unknown B	S	4.56	3.33	no
	Leoch	F	0.0293	0.0344	yes
	Leoch	S	0.0555	0.0558	yes
Water Rep/Con C	Locharbriggs	F	17.00	18.60	yes
	Locharbriggs	S	25.62	30.24	yes
	Clashach	F	26.02	21.95	no
	Clashach	S	21.65	25.51	yes
	Stainton	F	8.61	8.62	yes
	Unknown B	S	13.74	13.79	yes
	Leoch	F	0.0344	0.0405	yes
	Leoch	S	0.1052	0.0894	no
Water Rep. D	Locharbriggs	F	30.35	17.45	no
	Locharbriggs	S	16.00	25.81	yes
	Clashach	F	22.34	18.90	no
	Clashach	S	12.63	11.77	no
	Stainton	F	8.60	8.60	no
	Unknown B	S	3.9	23.90	no
	Leoch	F	0.1054	0.0345	no
	Leoch	S	0.1969	0.0895	no

Table 17 Change in pore size distribution between treated (external) and untreated (internal) sandstones samples from test panels. (PSD: pore size distribution)

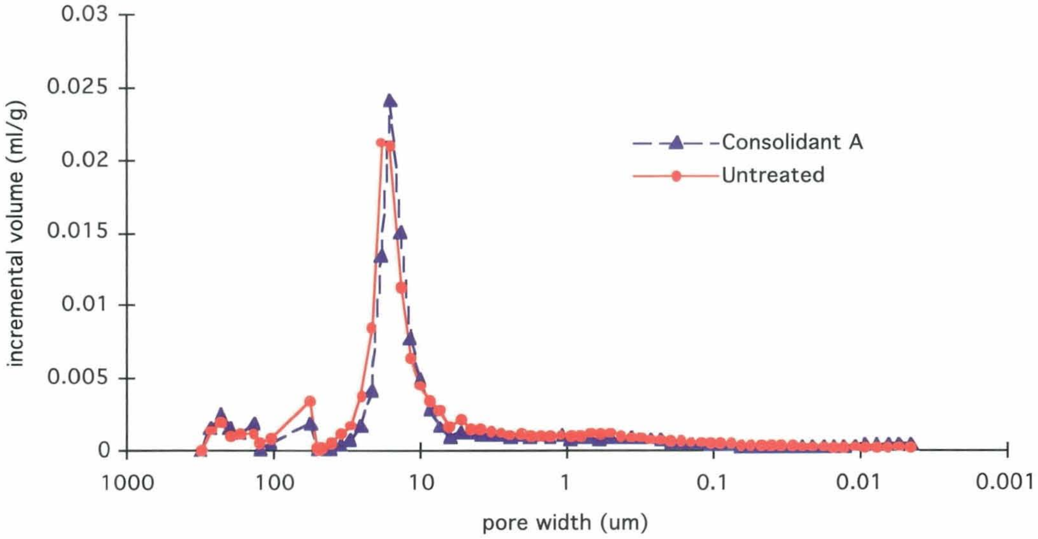


Figure 43a ***Fresh Locharbriggs sandstone****. Showing the pore size distribution of sandstones before (untreated) and after (treated) treatment with Consolidant A. Pore sizes given as diameter in microns (µm).*

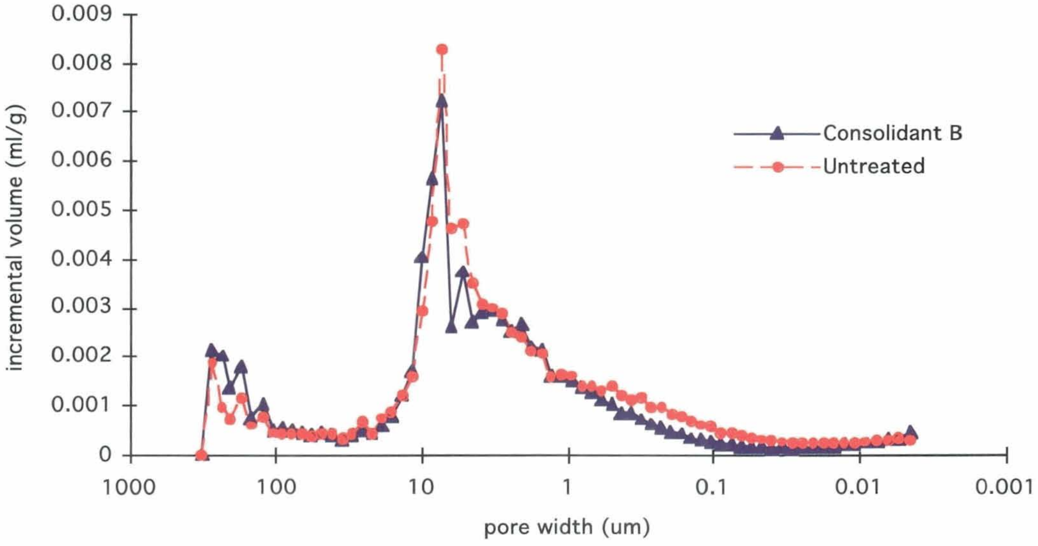


Figure 43b ***Fresh Stainton sandstone.*** *Showing the pore size distribution of sandstones before (untreated) and after (treated) treatment with Consolidant B. Pore sizes given as diameter in microns (µm).*

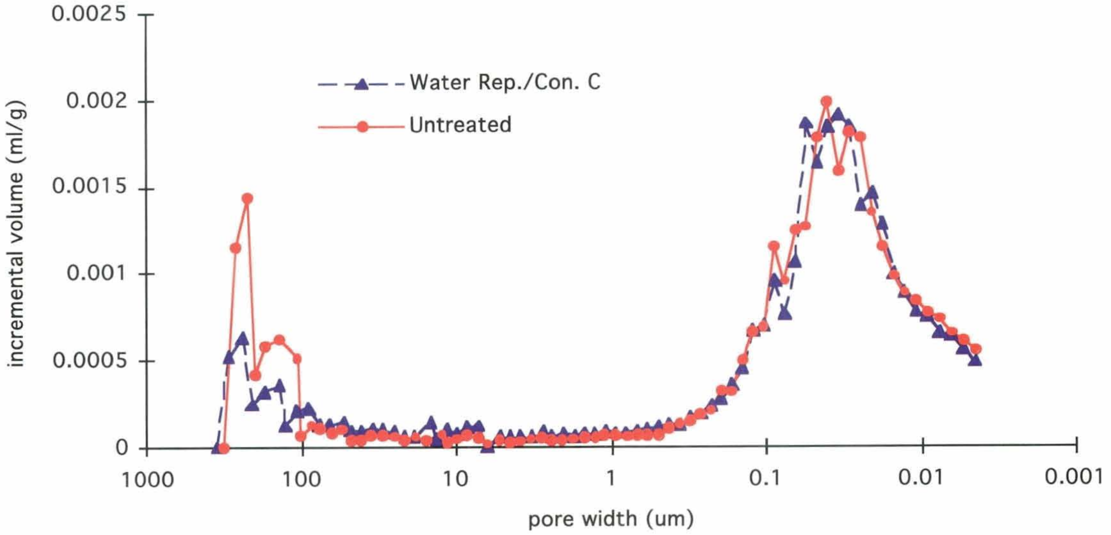


Figure 43c ***Fresh Leoch sandstone.*** *Showing the pore size distribution of sandstones before (untreated) and after (treated) treatment with Water Rep./Con. C. Pore sizes given as diameter in microns (μm).*

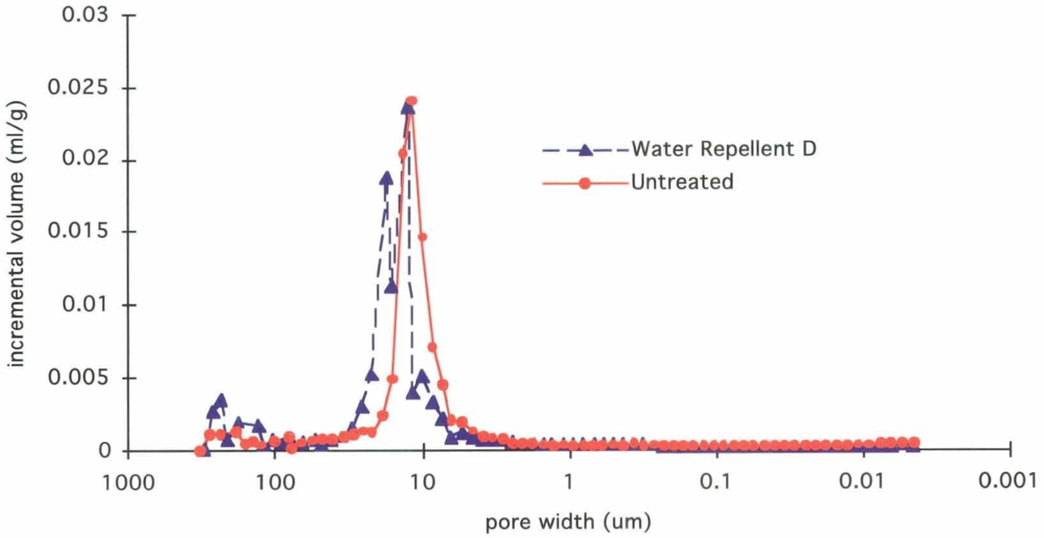


Figure 43d ***Soiled Clashach sandstone.*** *Showing the pore size distribution of sandstones before (untreated) and after (treated) treatment with Water Repellent D. Pore sizes given as diameter in microns (μm).*

The data in Table 16 show that, in general, there was no large difference in porosity between the treated exterior sandstone and the untreated interior sandstone. As would be expected, control samples showed only slight variations in internal and external porosity, either due to variations within the fabric of the stone itself or, in the case of soiled sandstones, variations caused by soiling or weathering effects. Taking means from all the sandstones (base of Table 16) does suggest that there was some overall reduction in porosity caused by treatments as the mean for the treated exterior of samples was, in all cases, lower than the untreated interior sandstone by between -2.9% and -0.6%. The difference in means on the control sample was only -0.2%. However, statistical analysis of the data (excluding Leoch sandstone) does not show any differences to be statistically significant (at 95% level). Results of two tailed *t*-tests were:

		p-value (2-tailed)
Control (untreated)	:	0.92
Consolidant A	:	0.24
Consolidant B	:	0.50
Water repellent/consolidant C	:	0.74
Water repellent D	:	0.69

On the panel treated with Water Repellent D soiled Locharbriggs sandstone showed a reduction in porosity of 5.6%, but since most other sandstones which received the same treatment showed no similar results, it is likely that the porosity difference was a result of weathering and/or soiling. Soiled Leoch sandstone consistently had a higher exterior porosity. This was most probably a weathering effect as this sandstone develops surface parallel cracks on weathering.

The data on pore size distribution (Figure 43 and Table 17) show some shifts in the distribution of porosity. On graphs of incremental porosity, as used in Figure 43, most sandstones show a single peak indicating the most common (mode) pore size in the stone. Partial in-filling of these pores would result in a reduction in the pore size and a shift in the position of this peak to a smaller pore diameter. Although the data in Table 17 indicate that many treatments caused an apparent reduction in the modal pore size, similar reductions were measured on both untreated control samples and on treated sandstones. Overall, results were rather inconclusive and it must be concluded that none of the tested treatments caused any significant changes in pore size distribution.

Calculations have been made of changes in the amount of porosity within particular size ranges. These data are shown in Table 18. The data are displayed graphically in Figure 43. The data indicate that where porosity was reduced following consolidant or water repellent treatment, most porosity was lost within the size range of 100-10 (m, although the treatment Water Repellent D appeared to cause no consistent losses in porosity. For Locharbriggs and Clashach sandstone, treatments Consolidant A, Consolidant B and Water Rep./Con. C caused porosity losses mainly in the range of 100-10 μm (with a relative increase in the percentage of smaller pores). Fresh Leoch sandstone showed little change in porosity and soiled Leoch sandstone apparently showed loss of porosity in the range of 0.1-0.01μm. However, it is likely that reduction in porosity in this size range was not due to the treatments but was only a change in percentage porosity relative to increases in larger pore sizes due to weathering - soiled (weathered) Leoch sandstone consistently has a higher porosity than fresh Leoch sandstone (Table 16). Fresh Stainton sandstone and its soiled pair (Unknown B) showed losses in porosity over a wider range of pore sizes from about 100-0.1 μm for treatments Consolidant A, Consolidant B and Water Rep./Con. C.

Size range (μm)	**Change in porosity on treatment (%)**				
Locharbriggs fresh	**None**	**Con. A**	**Con. B**	**Water Rep/Con C**	**Water Rep. D**
1000 - 100	-2.7	0.2	-0.5	-2.0	0.6
100 - 10	-1.2	-4.8	-7.0	-14.3	12.7
10 - 1	4.6	-3.2	2.7	0.6	-3.1
1- 0.1	4.8	-1.2	-0.7	-0.3	-2.6
0.1 - 0.01	-0.3	-0.3	-1.5	0.9	-2.2
0.01 - 0.001	-0.2	0.6	-0.3	0.7	-0.4
Locharbriggs soiled					
1000 - 100	5.0	-2.2	1.4	1.6	-0.5
100 - 10	-7.0	-7.0	-6.2	-15.8	-41.8
10 - 1	4.8	-1.0	14.0	9.1	10.3
1 - 0.1	0.4	-1.2	4.6	4.0	8.0
0.1 - 0.01	-0.3	-1.3	0.6	2.0	1.8
0.01 - 0.001	-0.2	-0.1	0.5	0.7	0.5
Clashach fresh					
1000 - 100	1.1	-2.5	-5.0	4.5	5.5
100 - 10	-7.2	-6.9	-11.4	-14.8	-2.4
10 - 1	0.6	-1.7	1.7	4.0	2.8
1 - 0.1	0.6	-0.1	1.0	2.3	1.8
0.1 - 0.01	0.0	-0.8	-0.4	-0.3	-0.5
0.01 - 0.001	-0.1	-0.2	-0.2	0.0	-0.3
Clashach soiled					
1000 - 100	-0.3	3.1	-4.8	-1.0	4.5
100 - 10	-5.1	-26.2	-16.2	-13.3	-1.3
10 - 1	0.5	3.7	5.0	1.6	-4.6
1 - 0.1	0.1	4.5	-0.8	0.1	-0.7
0.1 - 0.01	-0.5	1.6	-1.4	0.3	-1.9
0.01 - 0.001	-0.1	0.6	0.5	0.2	-0.7
Leoch fresh					
1000 - 100	-2.9	5.0	20.0	-7.1	10.8
100 - 10	-0.5	1.2	0.0	1.8	1.7
10 - 1	-0.7	-1.3	-0.2	1.1	2.1
1 - 0.1	0.5	-2.5	-2.8	0.0	18.9
0.1 - 0.01	0.5	-2.6	-0.7	0.8	-17.7
0.01 - 0.001	0.0	0.2	-0.4	-0.6	-0.1
Leoch soiled					
1000 - 100	0.7	9.9	0.1	12.8	-1.2
100 - 10	1.7	15.2	2.4	8.9	9.8
10 - 1	1.2	17.6	2.5	5.4	14.1
1 - 0.1	6.2	12.2	10.0	-3.2	13.4
0.1 - 0.01	-9.5	-32.5	-6.9	-7.0	-21.0
0.01 - 0.001	-0.2	0.8	-1.1	0.6	0.0
Stainton fresh					
1000 - 100	8.3	-3.3	3.8	0.9	0.9
100 - 10	-2.7	-12.0	2.1	3.2	3.2
10 - 1	*1.7*	*6.0*	*-5.4*	*-5.2*	*-5.2*
1 - 0.1	-0.3	-6.7	-5.0	-0.7	-0.7
0.1 - 0.01	-0.6	-1.2	-1.8	-1.1	-1.1
0.01 - 0.001	-0.3	0.3	0.1	-0.5	-0.5
Unknown B soiled					
1000 - 100	2.0	2.9	1.5	10.7	1.3
100 - 10	-1.3	-1.1	2.0	-7.0	0.3
10 - 1	-4.7	-9.7	4.5-	9.1	1.2
1 - 0.1	2.5	-10.5	-2.9	-3.5	1.2
0.1 - 0.01	-0.8	-0.2	-2.1	-0.2	-0.5
0.01 - 0.001	-0.3	0.5	-0.4	-0.1	-0.5

Table 18 Change in percentage of porosity within particular pore size ranges. The porosity of untreated sandstone is normalised to a total of 100%. The % porosity within each size range is calculated for both the untreated and the treated sandstone assuming the untreated value to be 100%. The table shows the difference in percentage porosity in each size range for the treated relative to untreated sandstone. Loss of porosity due to treatment is therefore shown as a negative value and vice versa. Data shown graphically in Figure 44

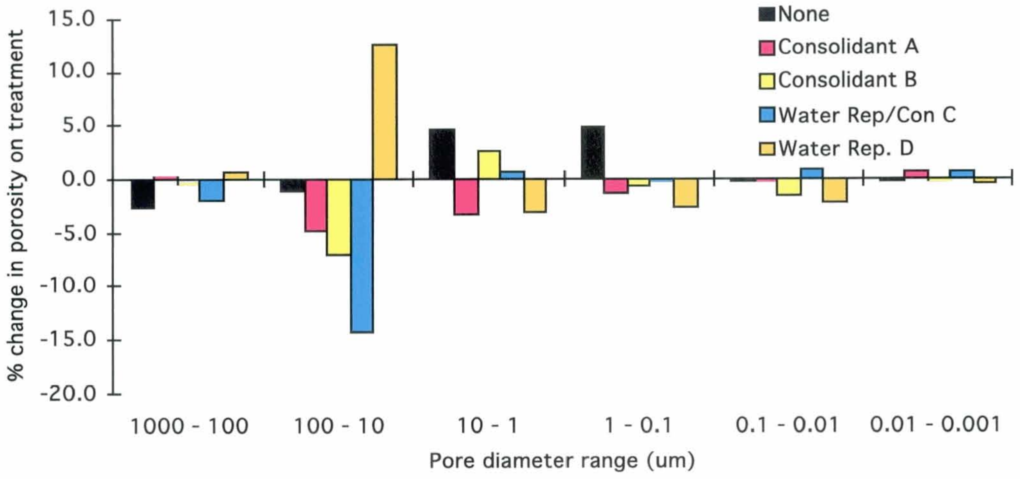


Figure 44a ***Fresh Locharbriggs sandstone****. Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

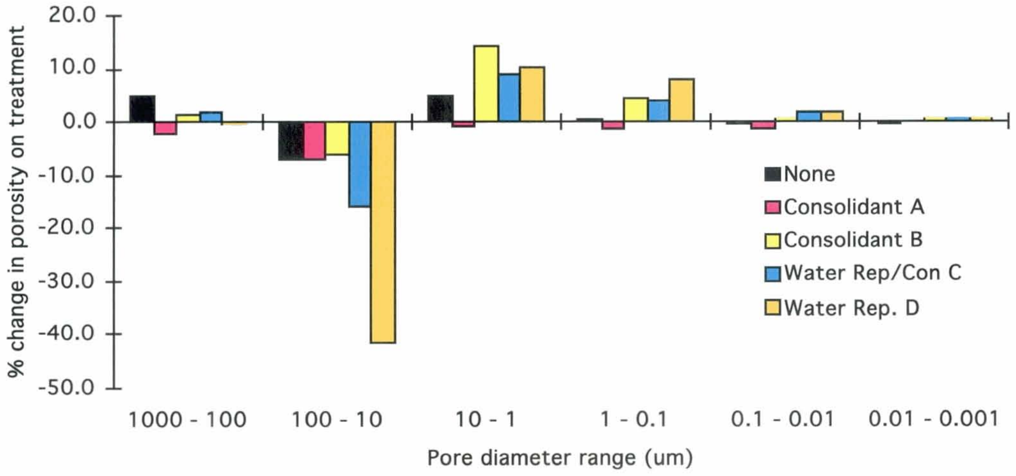


Figure 44b ***Soiled Locharbriggs sandstone.*** *Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

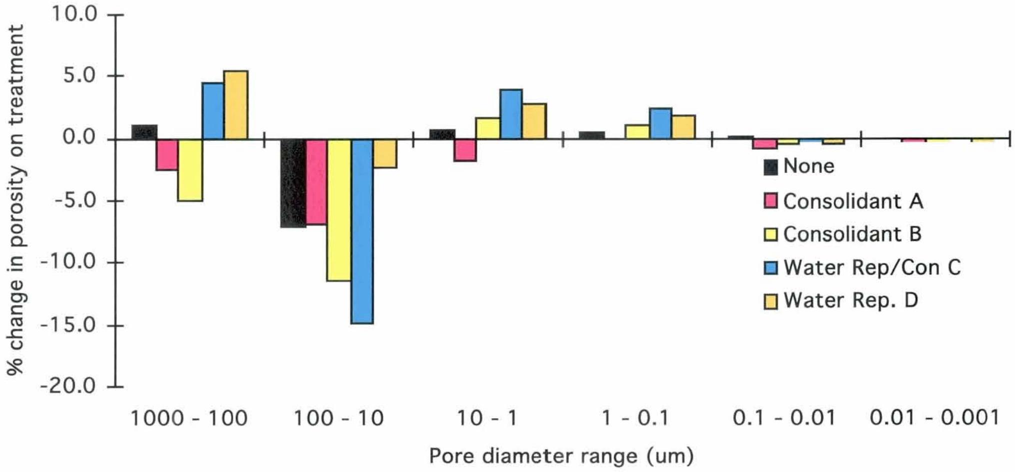


Figure 44c **Fresh Clashach sandstone**. *Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

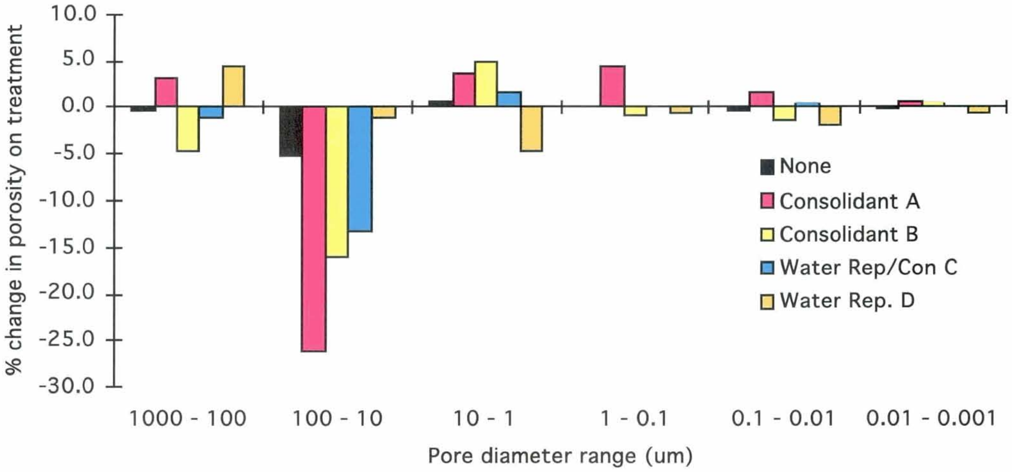


Figure 44d **Soiled Clashach sandstone.** *Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

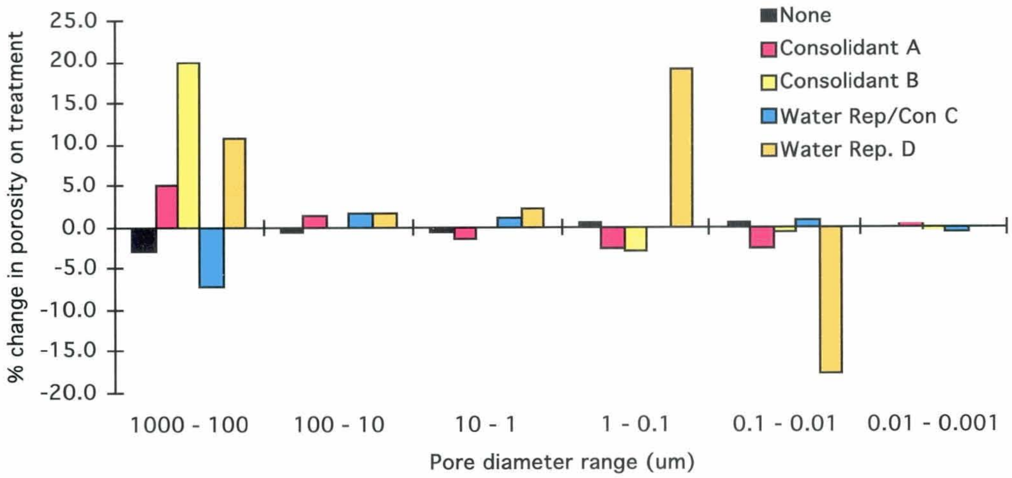


Figure 44e ***Fresh Leoch sandstone.*** *Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

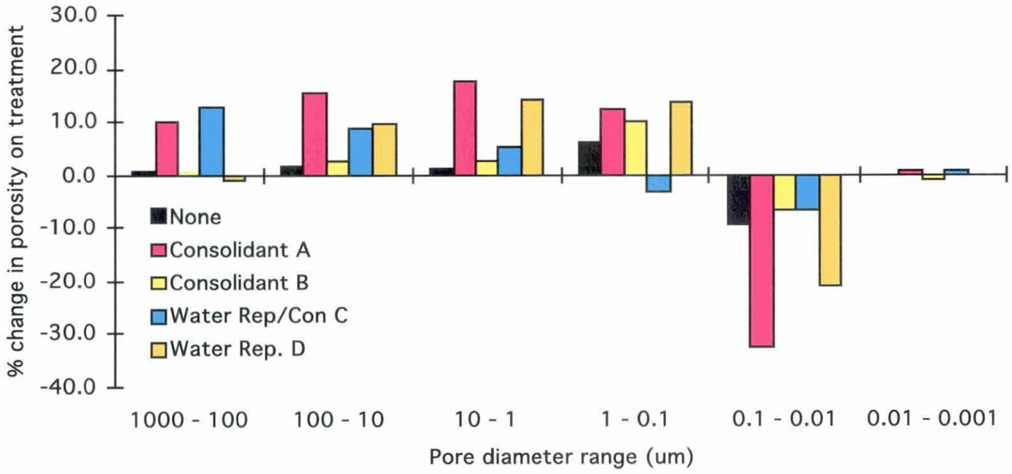


Figure 44f ***Soiled Leoch sandstone.*** *Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

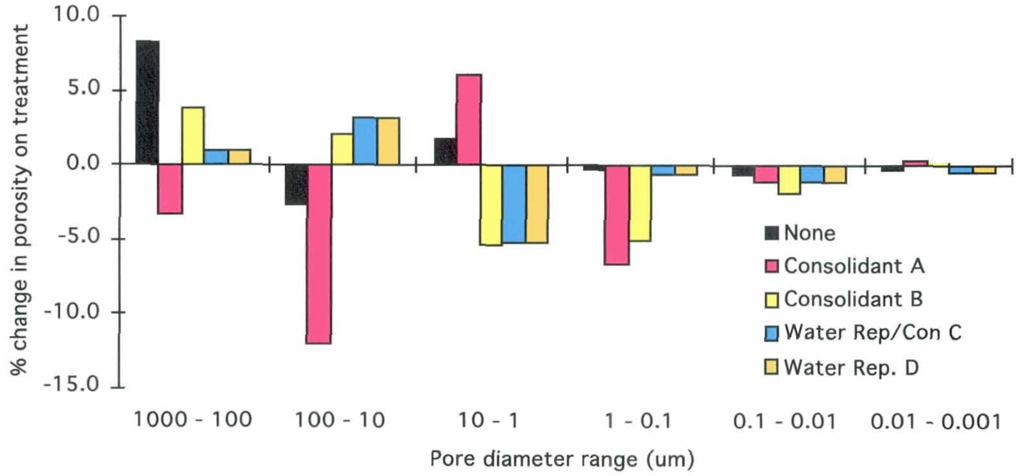


Figure 44g ***Fresh Stainton sandstone****. Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

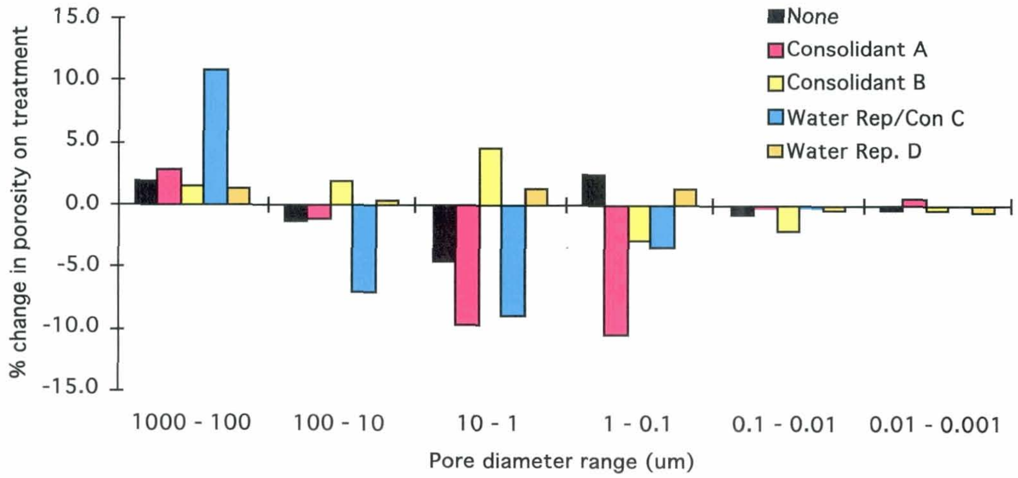


Figure 44h ***Soiled Unknown B sandstone****. Change in percentage of porosity within particular pore size ranges. Data from Table 18.*

4.4.11 Tomography

Impedance tomography can be used to identify the location of consolidants in controlled situations. Impedance tomography can map to location of dielectric properties that will be affected by the consolidants. A sample of Locharbriggs sandstone taken from the Water Rep./Con. C treated panel was tested using the procedure stated in Section 3.3.13. Figure 45 shows the results.

The results show that the consolidant has penetrated up to 70 mm into the core, and that the impedance effect is concentrated in the top 10 mm. The qualitative nature of this effect is difficult to determine and consolidant concentration is difficult to determine. The depth of 70 mm for the treatment is consistent with other depth tests.

4.5 Mortar test panels

4.5.1 Consolidant and water repellent treatment of mature mortar panels

Sandstone test panels were constructed for a previous research project on abrasive cleaning of sandstones in 1990. The mortar had therefore had 7-8 years to mature prior to these experiments. A selection of six panels containing three different mortars was chosen for application of consolidants and water repellents.

Lime mortar, 2 : 5 (lime : sand)	Normally used for stone types of poor durability.
Cement lime mortar, 1 : 3 : 12 (cement : lime : sand)	Normally used for less durable sandstone and limestones.
Cement lime mortar, 1 : 1 : 6 (cement : lime : sand)	Normally used for relatively impermeable stone types such as granite or basalt.

Four different water repellents/consolidants: Consolidant A (variety 1/2), Consolidant B, Water Rep./Con. C, Water Repellent D were applied to the panels using the same methodologies specified in Section 3 for the sandstone test panels. Each mortar panel was split into three zones of which the left and right were treated with a water repellent/consolidant and the central zone was left untreated (Figure 46). A sample of a silicone emulsion water repellent (Water Repellent E) was obtained during the research period and this was applied to an additional test panel (1:2:9 mortar mix). These panels have been used to look at the depth penetration of consolidants and water repellents into mortars of different composition.

4.5.2 Water drop tests

Cores from joints

The methodology for these water drop tests was the same as was specified in Section 3.3.5.1. Cores (25 mm diameter) were taken from joints in the mortar test panels after maturation of the treatments and were used water drop tests to determine the depth of penetration of treatments. Results are shown in Figure 47 and represent averages of several measurements. This test was successful in distinguishing the depth of penetration of water repellent treatments (Water Rep./Con. C, Water Repellent D and Water Repellent E) but was less successful for treatments which were not inherently water repellent (Consolidant A and Consolidant B). Results for the water repellent treatments have been summarised in Table 19. As can be seen both from the graphs (Figure 47) and table, the depth of penetration of the water repellent treatments was greater in the weaker mortar mixes than in the stronger.

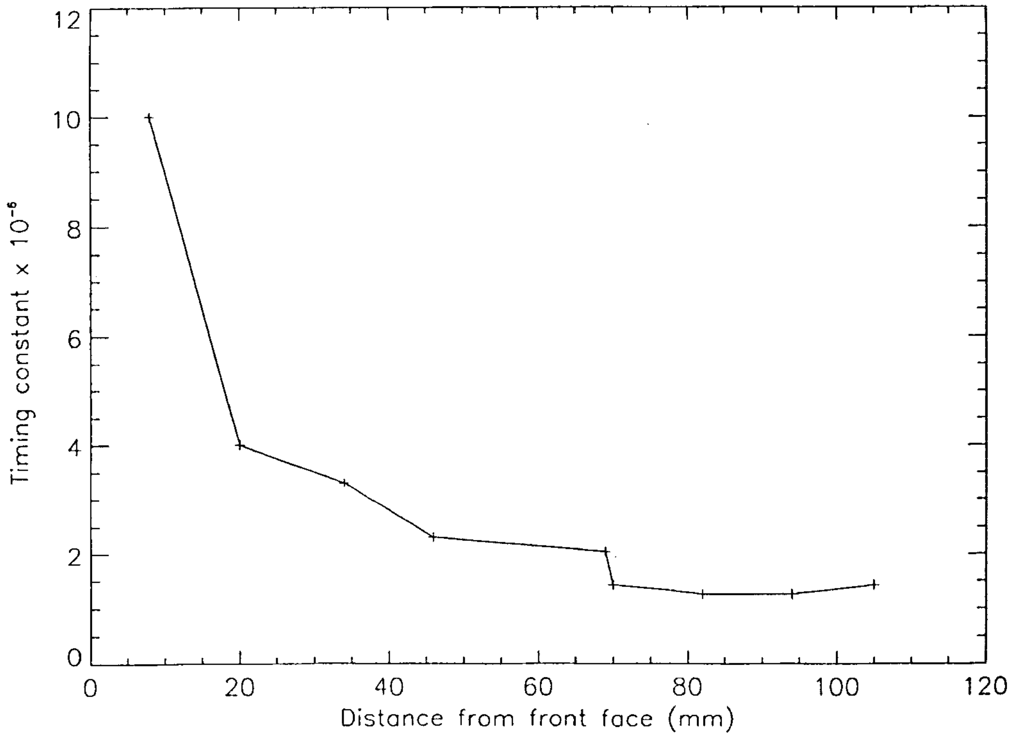
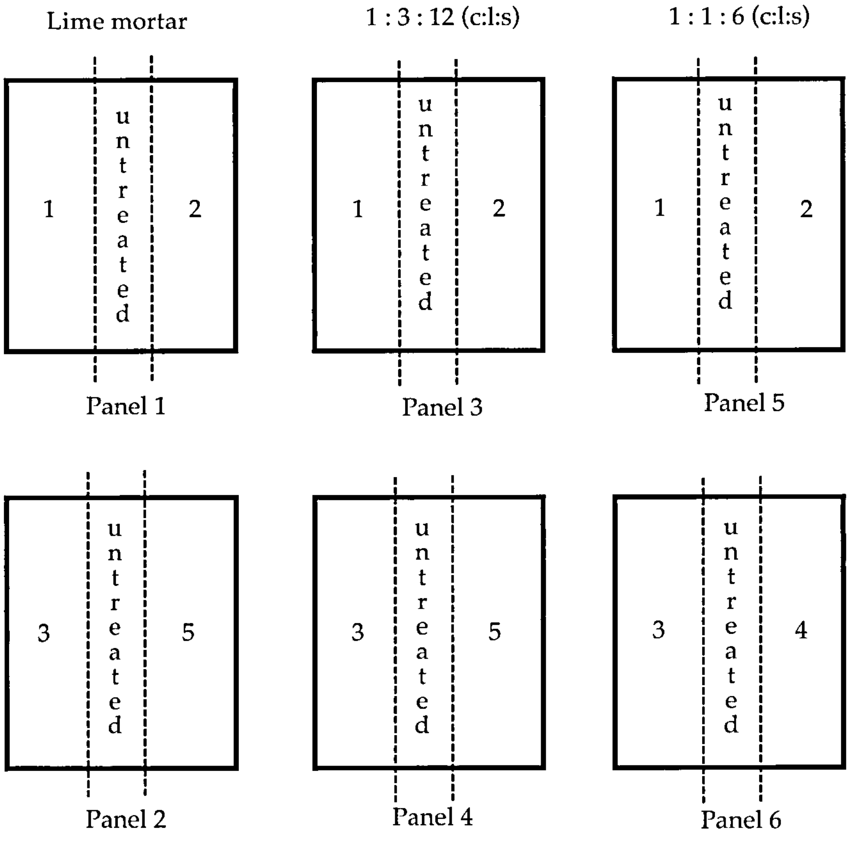


Figure 45 Change in timing constant by depth of treatment penetration for Water Rep./Con. C on Locharbriggs sandstone.



1: Water Repellent D

2: Water Repellent/Consolidant C

3: Consolidant B

4: Consolidant A (variety 1)

5: Consolidant A (variety 2)

Figure 46 Method of treatment of mortar test panels with consolidants and water repellents.

	Depth of penetration (mm) of mortar type			
Treatment	**lime**	**1:3:12**	**1:1:6**	**1:2:9**
Water Repellent D	70-80	20-30	10-30	-
Water Rep./Con. C	30-40	20-40	15-25	-
Water Repellent E	30-40	20-40	15-25	20-30

Table 19 Results of depth penetration measurement in joint mortar using water drop test.

Comparing the depths of penetration measured in mortar with those in sandstone (Section 4.4), the depth penetrations for Water Rep./Con. C and Water Repellent D treated mortar samples were:

lime mortar : roughly equivalent to Locharbriggs sandstone (porosity ~24%)
1:3:12 mortar : roughly equivalent to Stainton sandstone (porosity ~18%)
1:1:6 mortar : roughly equivalent to Clashach sandstone (porosity ~16%)
(sandstone porosity data from Section 4.4.10)

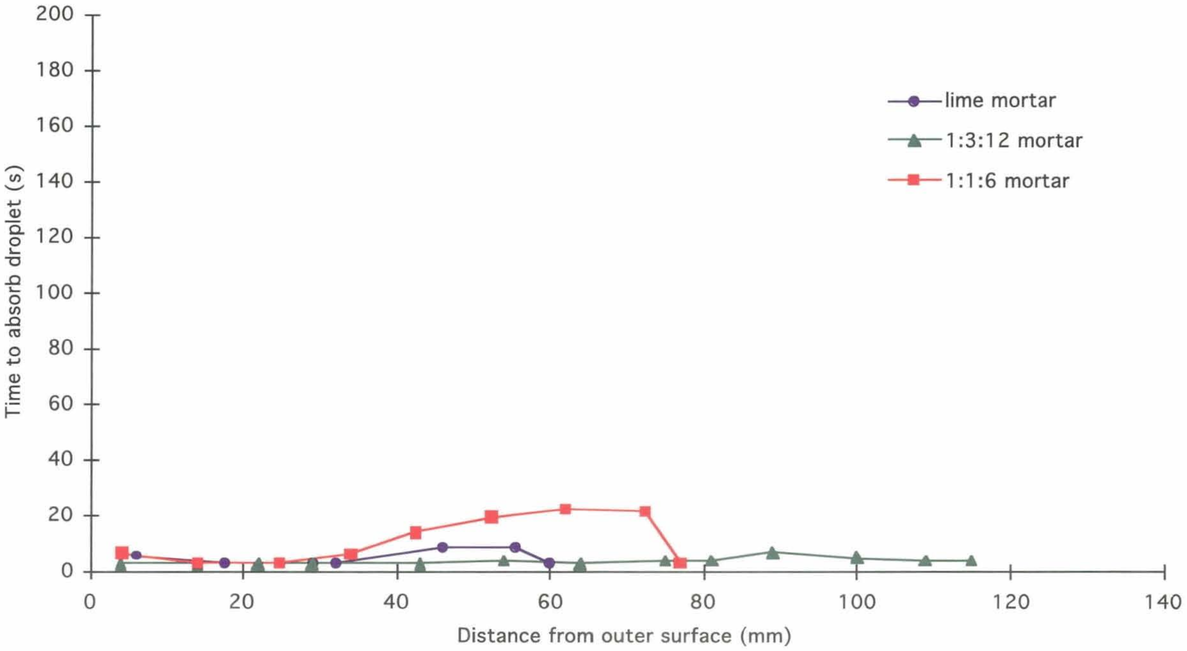


Figure 47a Depth of penetration of Consolidant A in different mortar types as measured by water drop test.

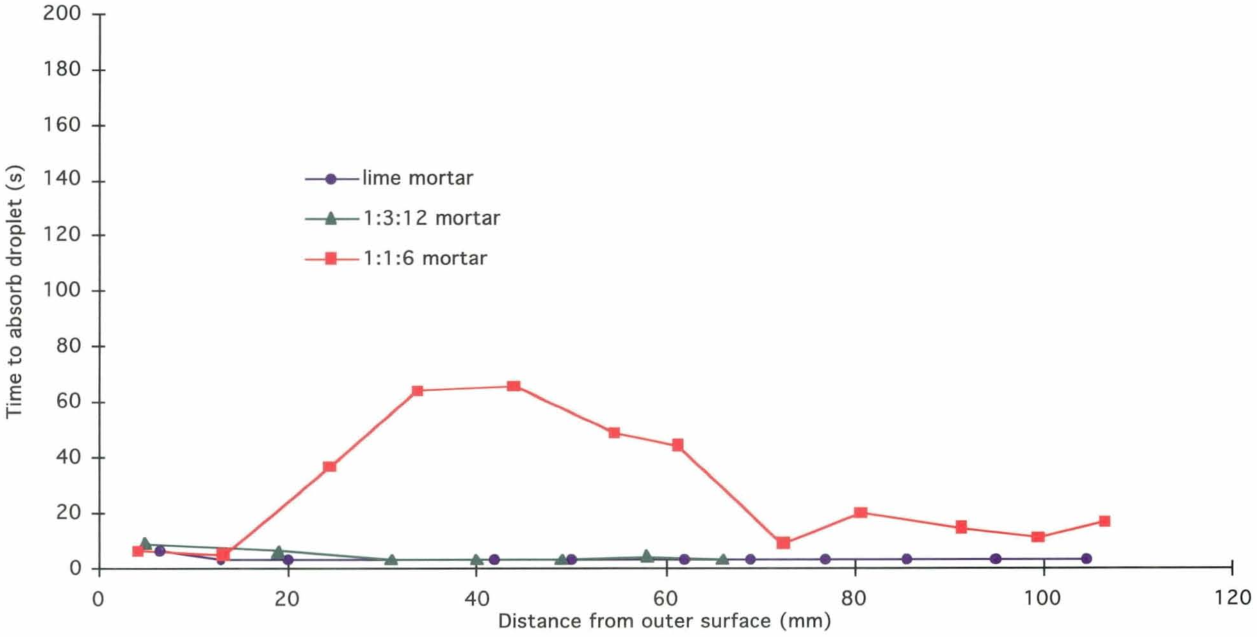


Figure 47b Depth of penetration of Consolidant B in different mortar types as measured by water drop test.

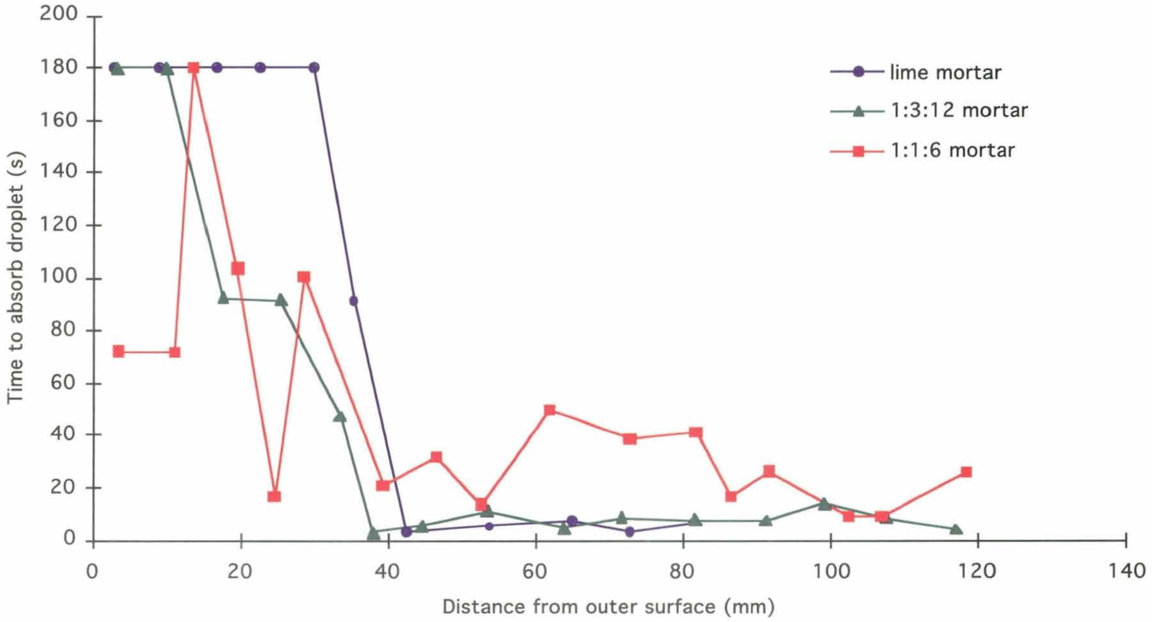


Figure 47c Depth of penetration of Water Rep./Con. C in different mortar types as measured by water drop test.

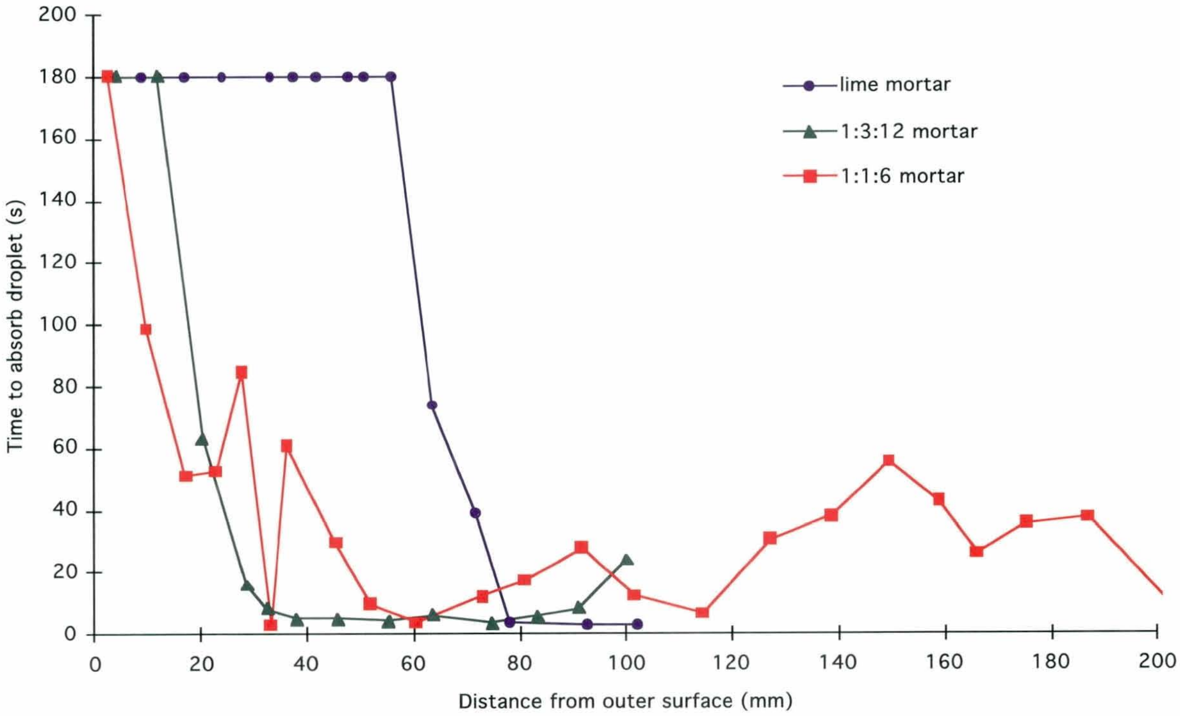


Figure 47d *Depth of penetration of Water Repellent D in different mortar types as measured by water drop test.*

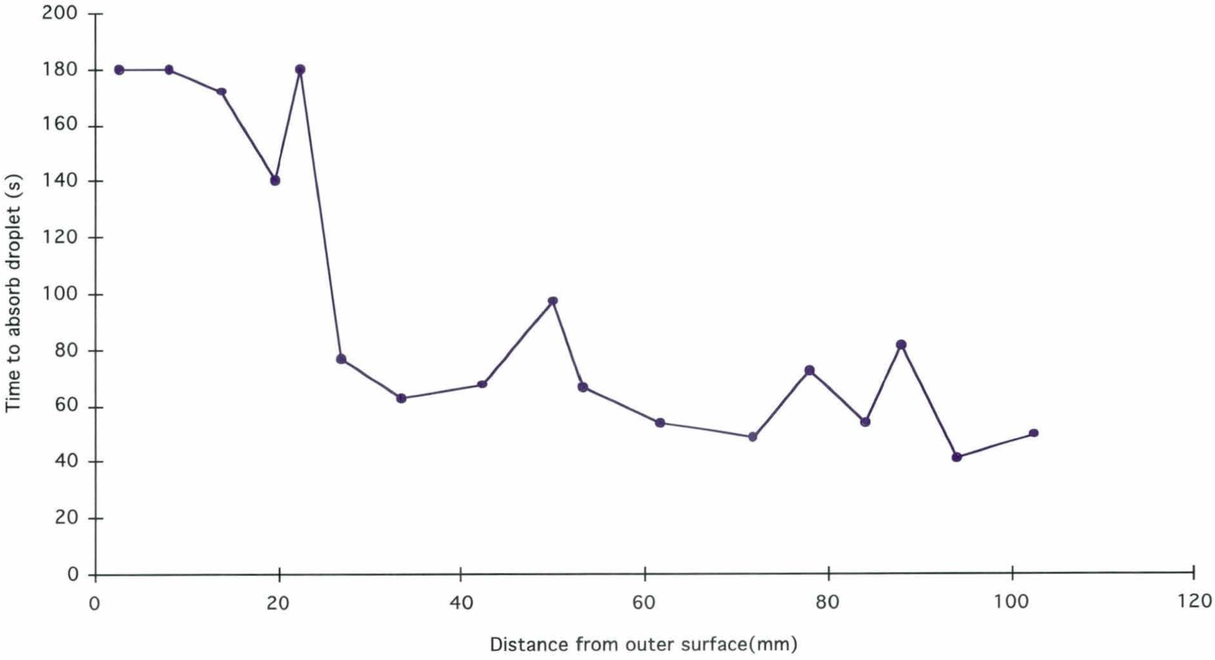


Figure 47e *Depth of penetration of Water Repellent E in 1:2:9 mortar as measured by water drop test.*

Cores along joints (sandstone + mortar)

The mortar test panels were also cored along joints, obtaining cores which included both sandstone and mortar. This allows for comparison of the penetration of the treatment in mortar and sandstone adjacent to the plane of the joint as it is possible for the penetration of the treatment to differ between the two media. The results for depth penetration of water repellent treatments (Water Repellent D and Water Rep./Con. C) in mortar and sandstone adjacent to joints (as measured by water drop tests) are shown in Figure 50. These graphs are averages from several measurements. For the least durable mortar (lime), penetration of the treatments (Table 20) Water Rep./Con. C and Water Repellent D went deeper into the mortar than into the sandstone (moderately porous sandstone of about 15% porosity). For the 1:3:12 mortar Water Rep./Cons. C went slightly deeper in the mortar but Water Repellent D penetrated to about the same depth in sandstone and mortar. For the most durable mortar (1:1:6), penetration of the water repellent treatments Water Rep./Con. C and Water Repellent D was greater in the sandstone than in the mortar.

	Depth of penetration of treatment (mm)					
Treatment	**In lime mortar**	**In sandstone**	**In 1:3:12 mortar**	**In sandstone**	**In 1:1:6 mortar**	**In sandstone**
Water Rep./Con. C	20-30	15-25	15-35	10-25	10-20	20-30
Water Rep. D	40-80	20-50	15-35	15-35	10-20	15-30

Table 20 Depth of penetration of water repellent treatments into mortar and sandstone adjacent to joints.

Penetration of treatments varied from sample to sample and within samples. It was noticeable that in some cases the water repellent treatment had ìtracked inî along the joint between the sandstone and the mortar (Figure 48). This was observed in some cores which were taken from the upper edge of sandstone blocks, but was not observed where the core was taken from the edges or base of sandstone blocks. This suggests that the phenomenon occurs due to treatment run-off over the wall surface pooling on the top edge of sandstone blocks and being drawn in along cracks between the mortar and stone as is illustrated in Figure 49.

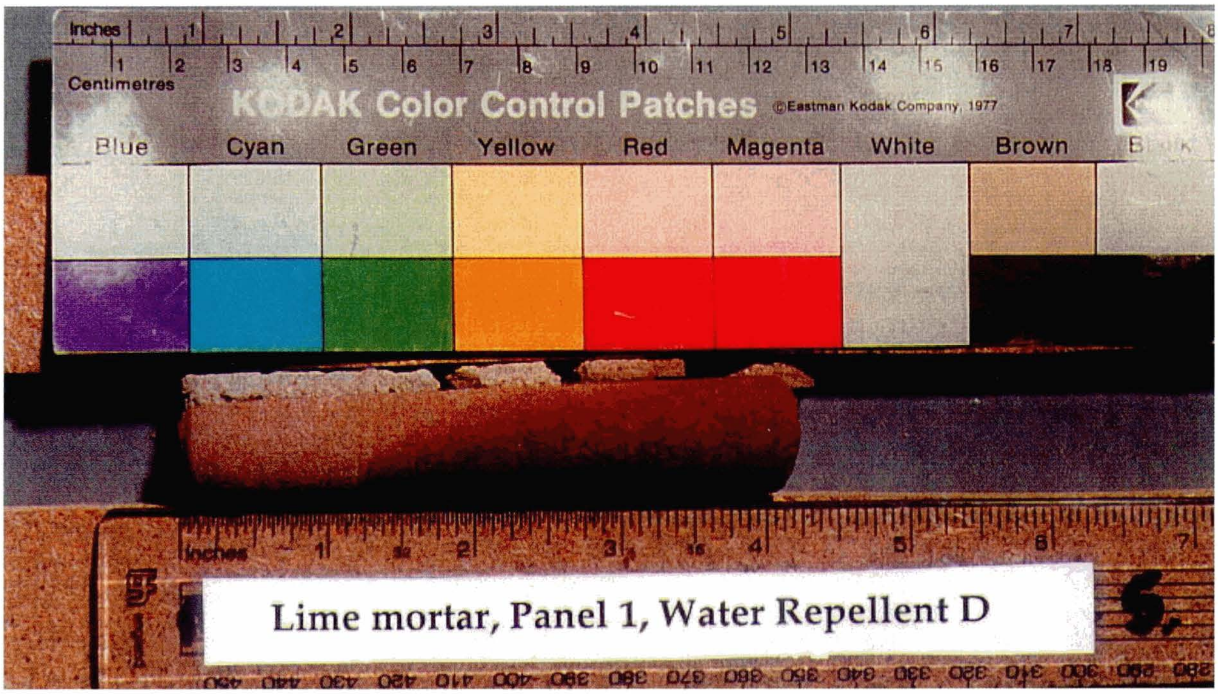


Figure 48 Photograph showing the water repellent treatment being drawn in along the joint between sandstone and mortar.

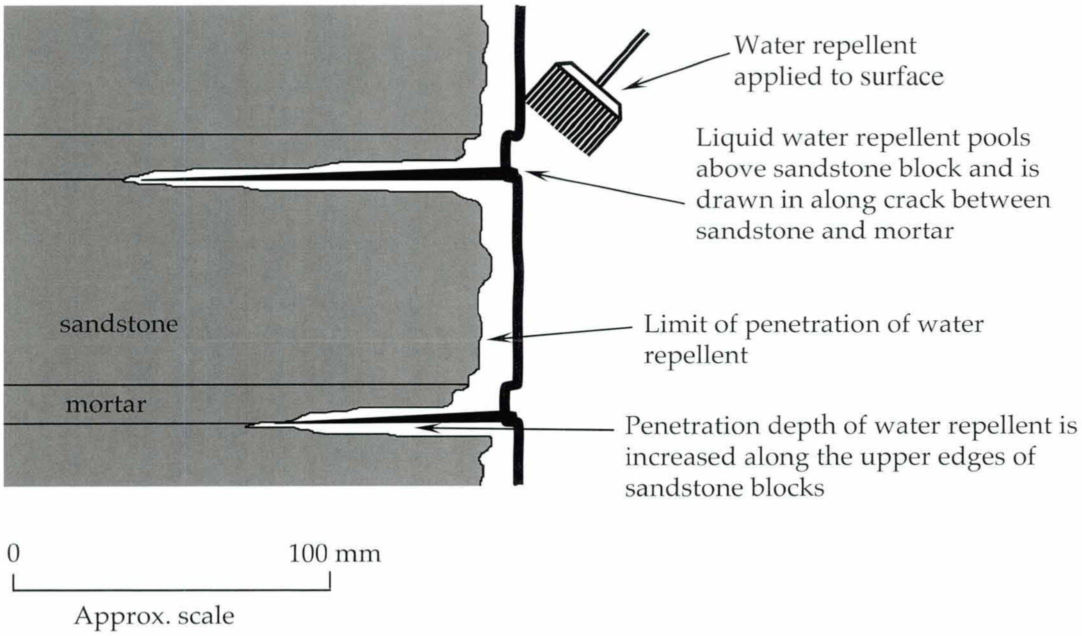


Figure 49 Diagram showing possible mechanism for water repellent "tracking in" along joints between sandstone and mortar.

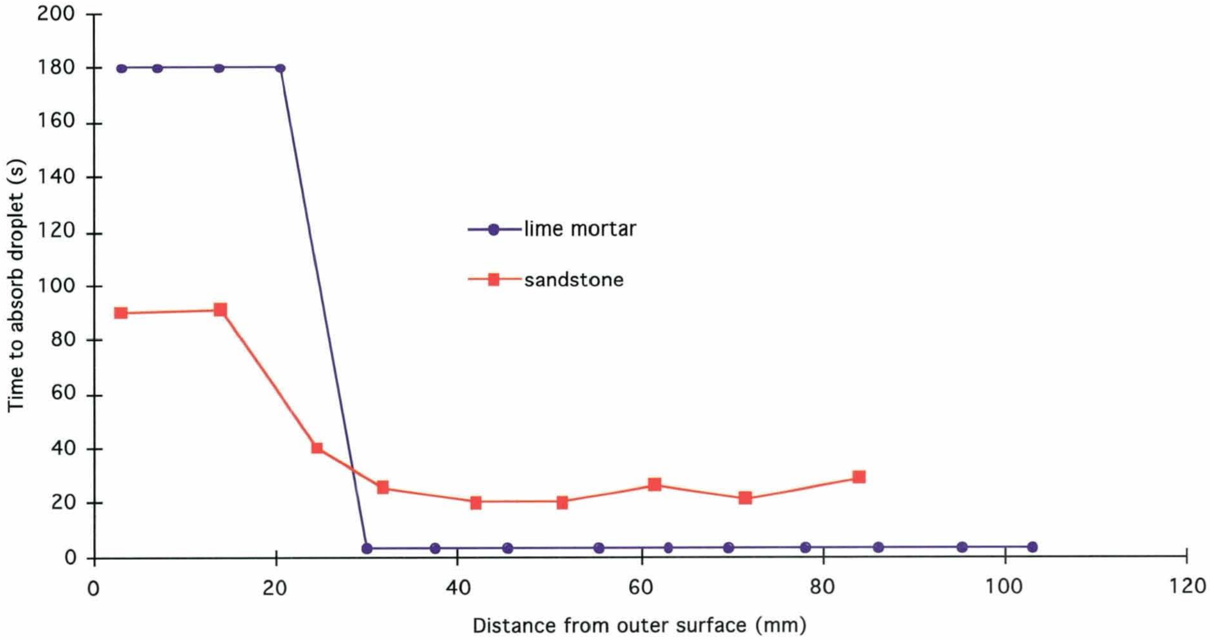


Figure 50a Depth of penetration of Water Rep./Con. C into lime mortar and sandstone adjacent to a joint as measured by water drop test.

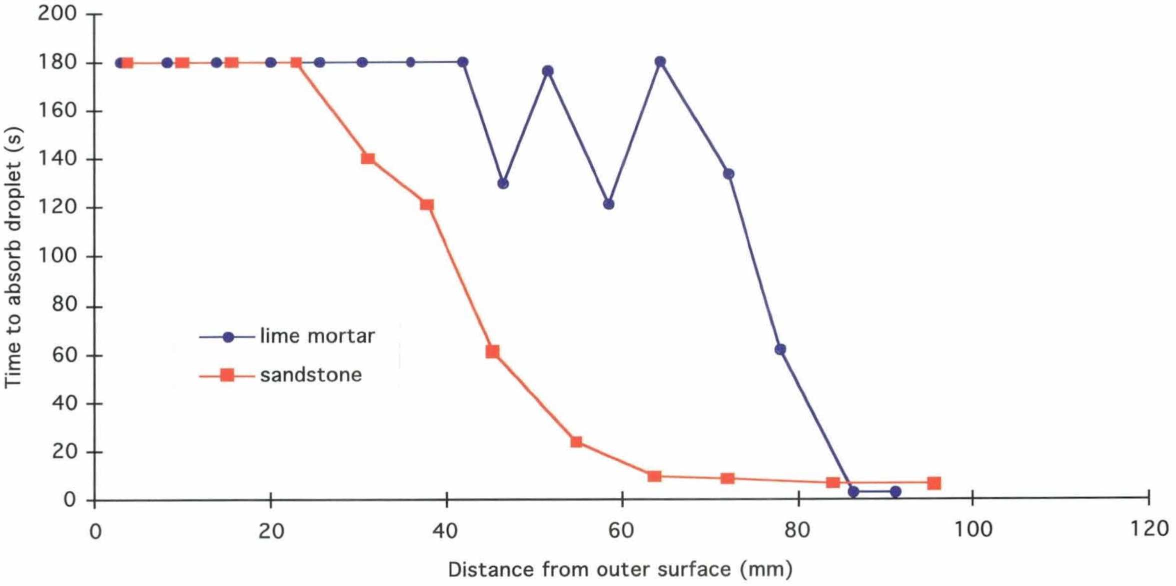


Figure 50b Depth of penetration of Water Repellent D into lime mortar and sandstone adjacent to a joint as measured by water drop test.

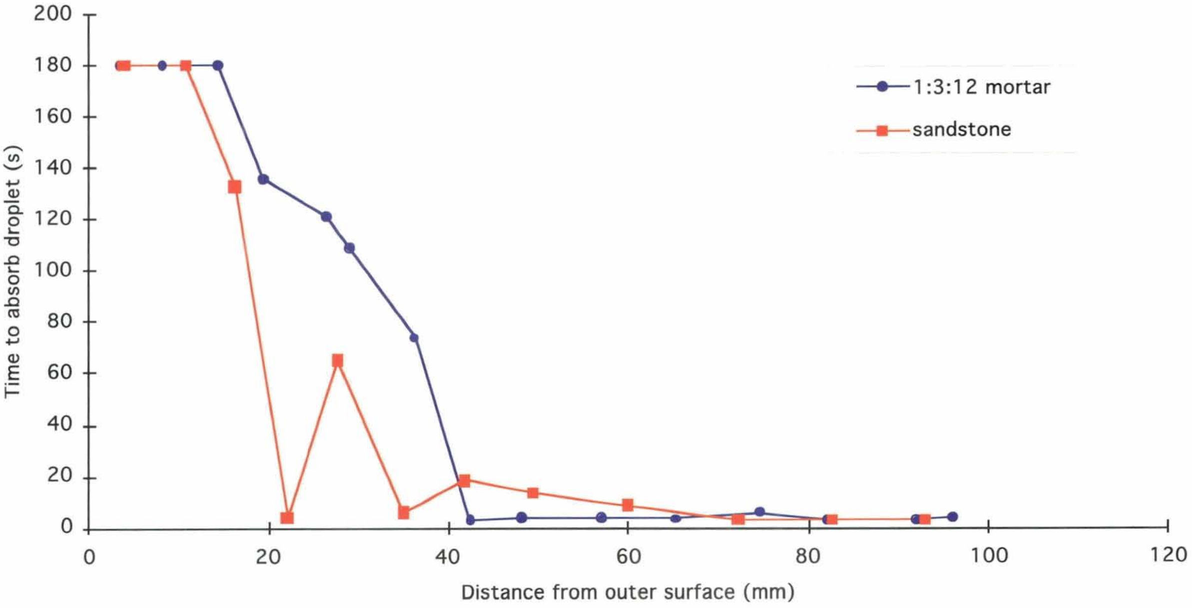


Figure 50c Depth of penetration of Water Rep./Con. C into 1:3:12 mortar and sandstone adjacent to a joint as measured by water drop test.

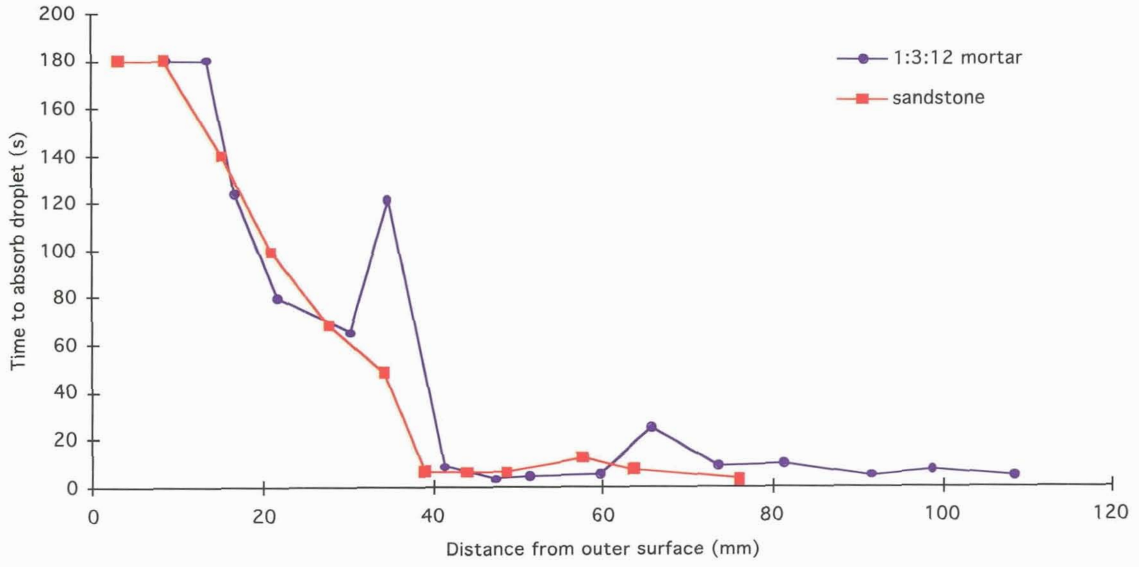


Figure 50d   Depth of penetration of Water Repellent D into 1:3:12 mortar and sandstone adjacent to a joint as measured by water drop test.

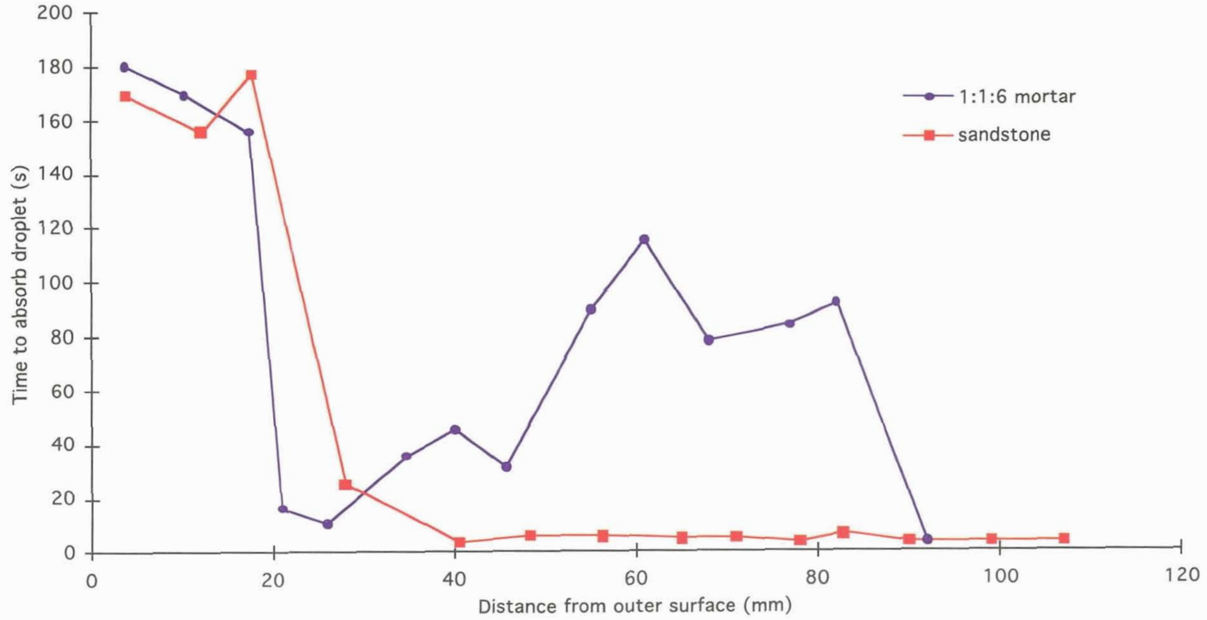


Figure 50e   Depth of penetration of Water Rep./Con. C into 1:1:6 mortar and sandstone adjacent to a joint as measured by water drop test.

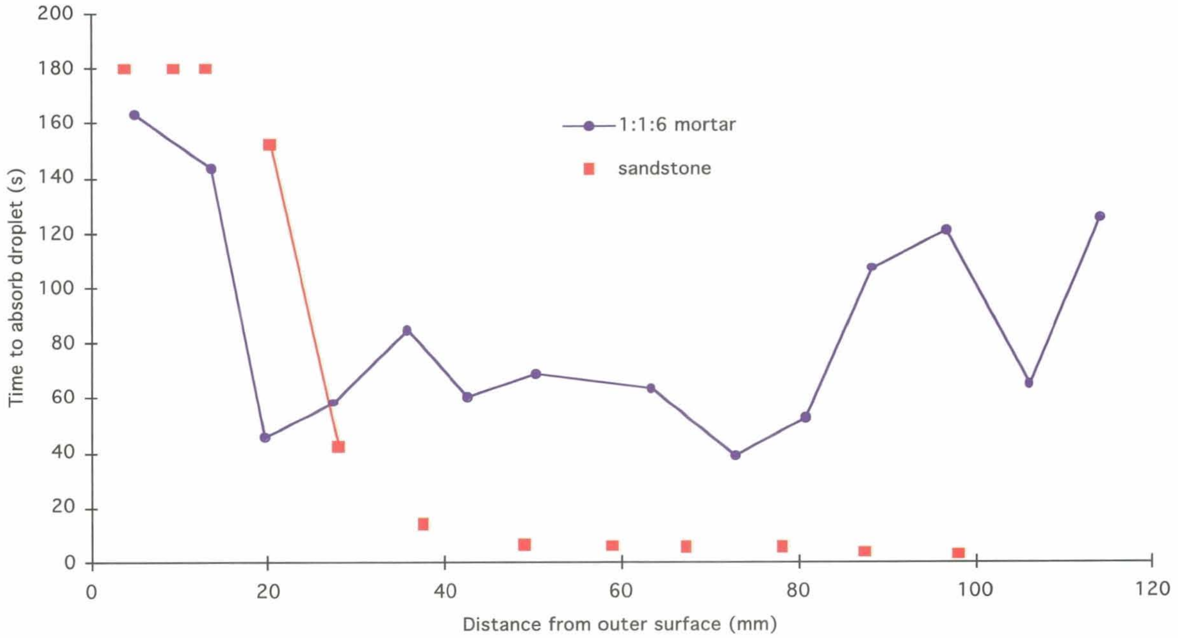


Figure 50f Depth of penetration of Water Repellent D into 1:1:6 mortar and sandstone adjacent to a joint as measured by water drop test.

Mortar cubes

Mature cubes of mortar (10 cm^3) were treated with consolidants and water repellents at the same time as the test panels. The cubes were mortared in place at the top of the test panels at the time of their construction (1990) and have remained in place, without any further treatment, since that time. In each case the front face of the cube was treated at the same time and using the same methodology as the rest of the panel. Untreated cubes were used as controls. These cubes were examined to determine penetration of treatments into mortar in the absence of any effects from joints or surrounding sandstone.

Examination of water soaked, sliced cubes (Figure 52) and water drop absorption measurements (Figure 51) revealed the depth of penetration of the water repellent treatments. While the depth of penetration of water repellent treatments can be observed on wetted, cut sections of the cubes, measurement of depth penetration by water drop absorption was more problematic. Problems were caused by apparent differences in the density across the mortar cubes which strongly affected water drop absorption. A summary of the data showing depth of penetration of water repellent treatments into the mortar cubes is given in Table 21.

	Depth of penetration (mm) Mortar			
Treatment	**lime**	**1:3:12**	**1:1:6**	**1:2:9**
Water Repellent D	5-10	10-15	<5	nd
Water Rep./Con. C	5-10	15-25	5-10	nd
Water Repellent E	nd	nd	nd	5-10

nd: no data

Table 21 Results of depth penetration measurement in mortar cubes using water drop test.

For non-water repellent treatments (Consolidant A and Consolidant B) the water drop test was unable to distinguish any differences between treated and untreated areas of mortar. The apparently high degree of water repellency in the centre of lime cubes (especially in the case of Consolidant B) was not an indication of water repellency due to treatment, but was caused by variation in the compaction of the lime mortar.

The effects of variable compaction in the lime mortar were also visible on the water repellent treated cubes (Water Rep./Con. C and Water Repellent D). The water repellent zones on these cubes were confined to about 5-10 millimetres below the outer surface. This is very different from the results obtained in joint mortar where depths of penetration of 40-80 mm were observed.

For the 1:3:12 mortar the depth of penetration of Water Rep./Con. C and Water Repellent D was greater than their penetration in lime mortar (Table 21 and Figure 51). This contrasts with the results obtained for penetration of these treatments into the joint mortars (Table 20) where the lime mortar absorbed these treatments most deeply.

For the 1:1:6 mortar the depth of penetration of Water Rep./Con. C and Water Repellent D in the mortar cubes was lower than that in lime or 1:3:12 mortar (Table 21 and Figure 51). This is consistent with results obtained with cores taken from joint mortar (see above) where water repellent penetration was also found to be lowest in the 1:1:6 mortar, this being the densest mortar mix tested. However, the depth of penetration measured in test cubes was significantly lower than that measured in joint mortar (Table 20).

These results indicate that tests of water repellent penetration carried out on mortar test cubes may not accurately simulate their likely penetration in mortar joints on a building facade. The greater bulk of mortar in the test cubes results in a situation where the packing, setting and carbonation of the mortar may not closely simulate the characteristics of mortar in relatively thin joints. Additionally, on a building facade, and especially where cement mortars have been used, there is likely to be cracking at the bond between mortar and stone. Results from coring of joints (see above) indicated that water repellents can be drawn into the joint by capillary forces along cracks. In some cases this may be the dominant factor with respect to depth of penetration of treatments into mortar resulting in a greater depth of penetration than would have been predicted from results in bulk mortar.

Freshly cut sections across the cubes were treated with phenolphthalein to test for the depth of carbonation (Figure 53). Results showed that the depth of penetration of consolidants and water repellents was not the same as the depth of carbonation.

	Carbonation depth
Lime mortar	5-31 mm
1:3:12 mortar	12 mm to complete
1:1:6 mortar	12-50 mm

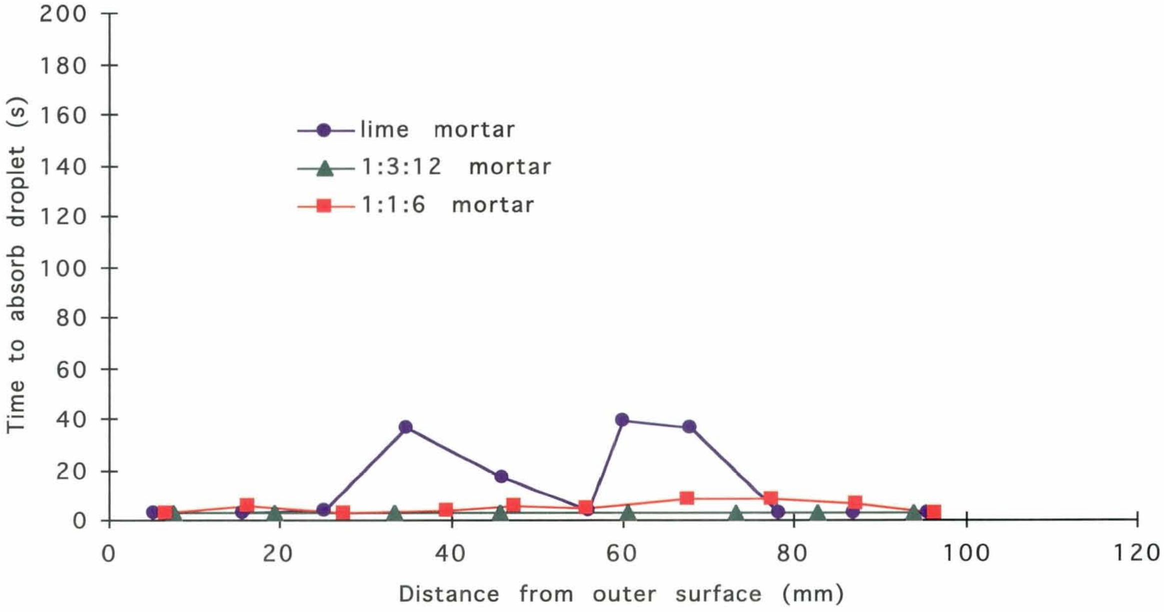


Figure 51a Depth penetration of Consolidant A (var. 1: lime & 1:3:12, var. 2: 1:1:6) on cut face of mortar cubes as measured by water drop absorption rates.

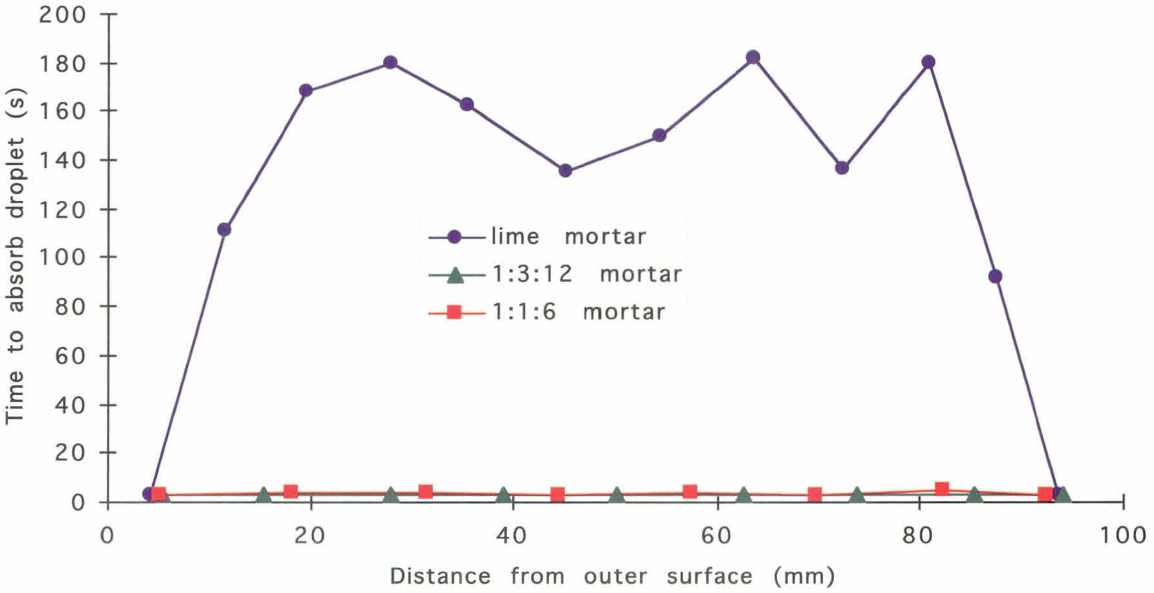


Figure 51b Depth penetration of Consolidant B on cut face of mortar cubes as measured by water drop absorption rates.

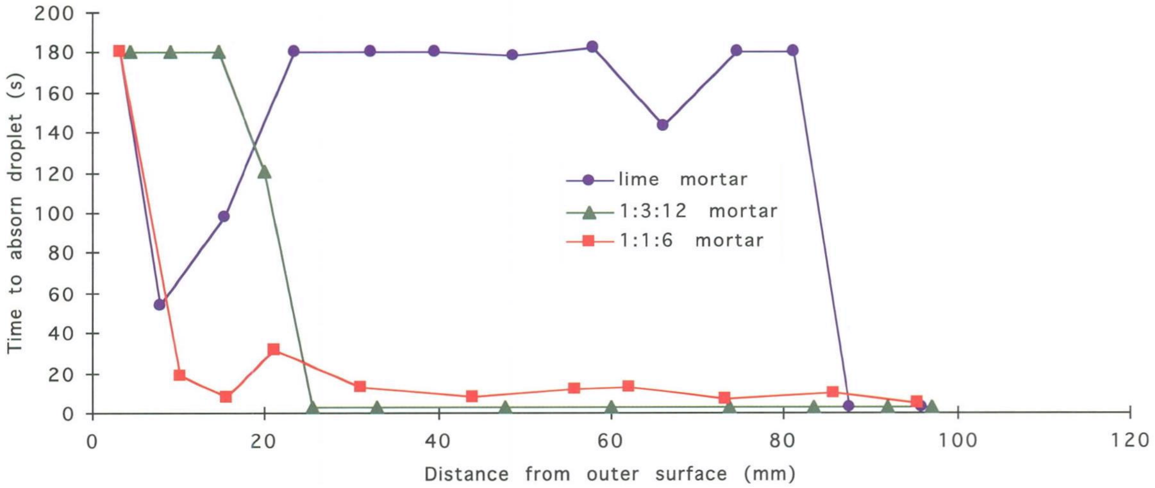


Figure 51c Depth penetration of Water Rep./Con. C on cut face of mortar cubes as measured by water drop absorption rates.

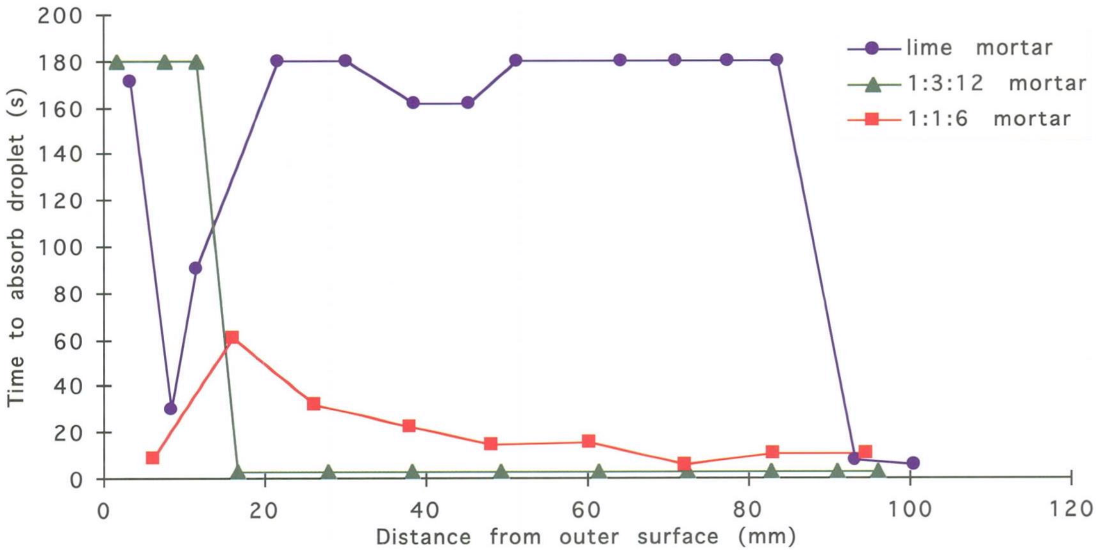


Figure 51d Depth penetration of Water Repellent D on cut face of mortar cubes as measured by water drop absorption rates.

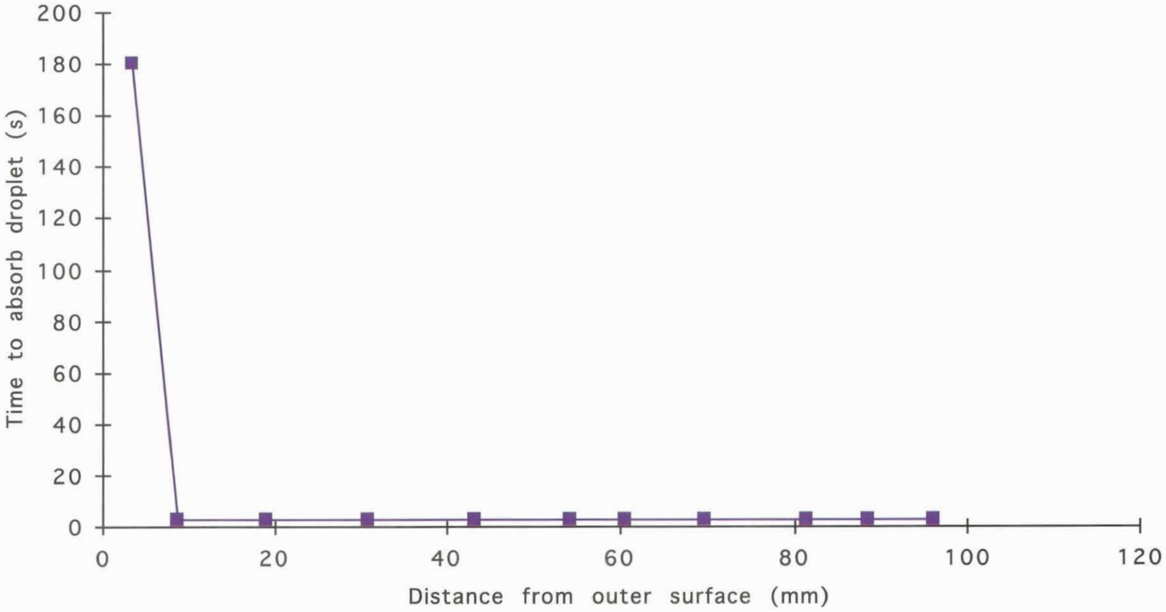


Figure 51e Depth penetration of Water Repellent E on cut face of mortar cube as measured by water drop absorption rates.

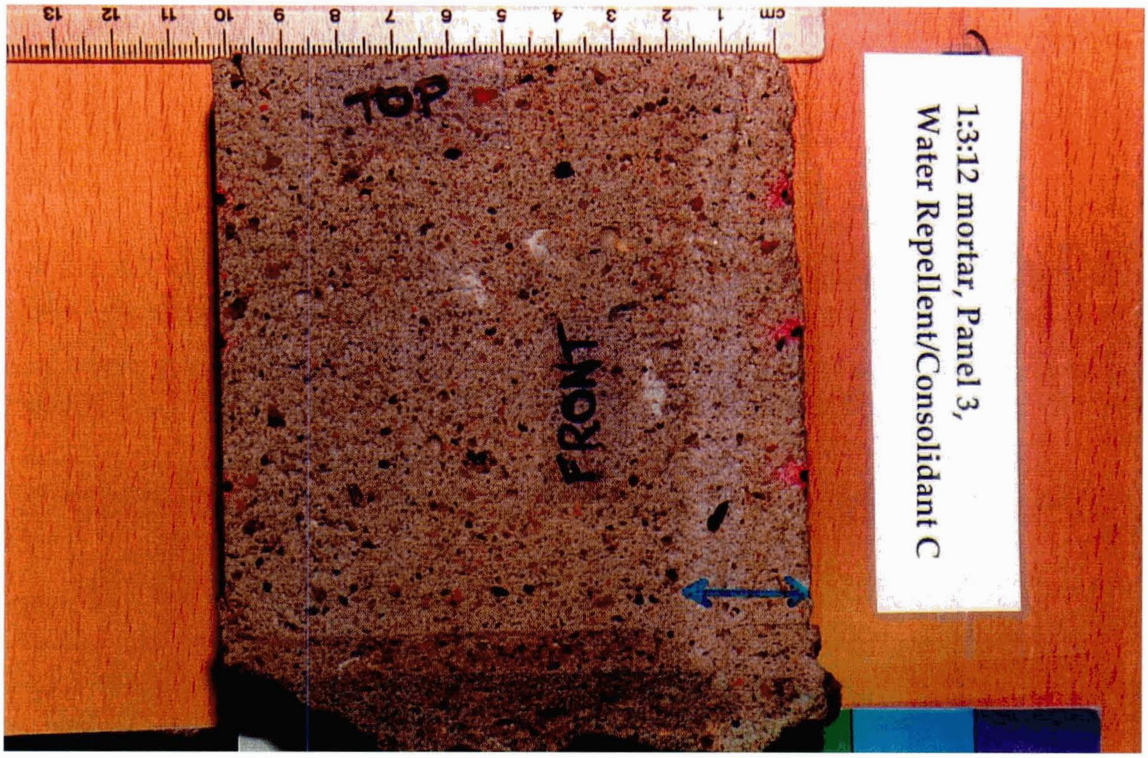


Figure 52 Photograph of wetted, cut face of mortar cube showing depth of water repellency.

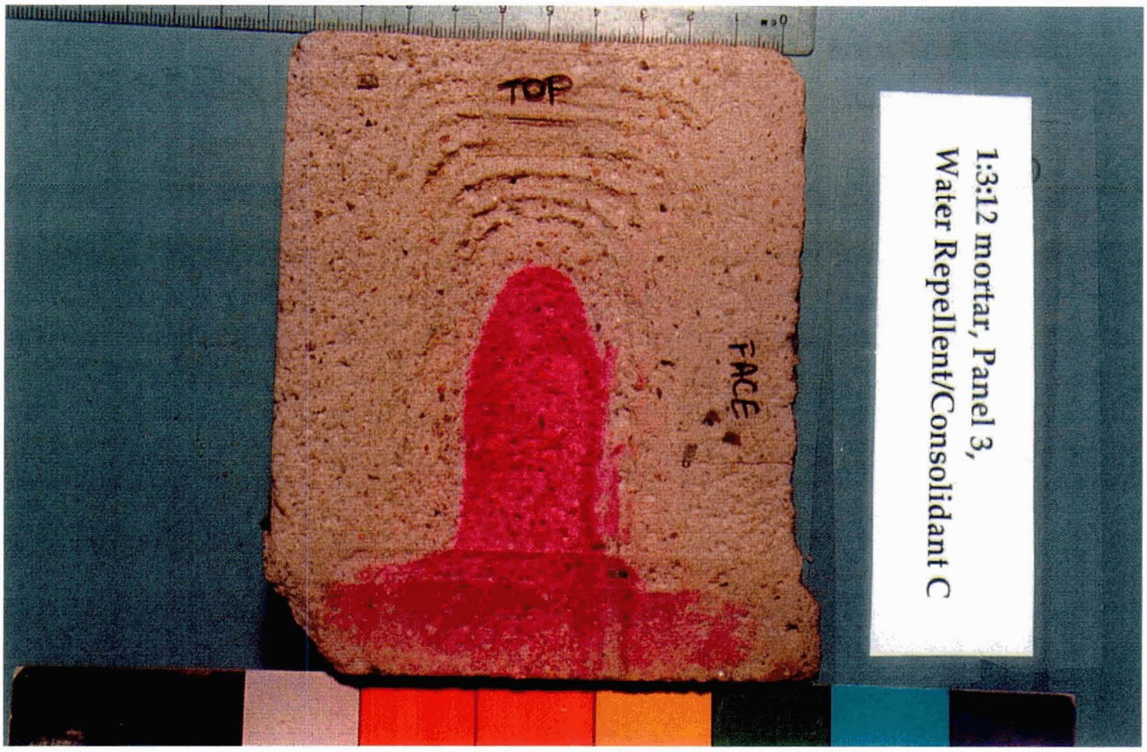


Figure 53 Photograph of phenolphthalein treated cut face of 1:3:12 mortar cube (previously treated with Water Rep./Con. C) showing depth of carbonation.

4.5.3 Mercury porosimetry of mortars

Mercury porosimetry analysis of mortar samples was carried out on treated test panels containing mature mortars (Section 4.5.1). Cores were taken from treated areas of the test panels and from untreated control areas on the same panels. Both external (treated and/or weathered) and internal (untreated) samples were assessed from each core. Due to the large amount of data only selected results are shown graphically in Figure 54, but the complete results from measurements of porosity are shown in Table 22.

The data in Table 22 show a wide degree of variability in both treated and untreated samples. While the treated exteriors of the samples often had a lower porosity than the untreated interiors (as would be expected if treatment had resulted in loss of porosity), the control samples gave similar results. This indicated that the observed porosity differences may be an effect of weathering or working rather than the consolidants and water repellents. The degree of variability in mortar porosity makes it difficult to determine any trends attributable to treatment in this relatively small sample.

Table 23 shows the measured changes in pore size distribution for external (treated/weathered) and internal (untreated) samples of mortar. Figure 55 and Table 24 show the changes in porosity within particular pore size ranges (as described in Section 4.4.10, Table 18). Again, for both these data sets, there was no significant difference between the untreated control samples and the samples treated with consolidants or water repellents.

In conclusion, due to the high variability of porosity in the mortars, no conclusive information could be obtained regarding the effects of consolidant and water repellent treatments on porosity of mortars.

In Section 4.5.2 the depth of penetration of water repellent treatments in mortar was compared to that in sandstones. It was found that penetration depths were:

lime mortar:	roughly equivalent to Locharbriggs sandstone
1:3:12 mortar:	roughly equivalent to Stainton sandstone
1:1:6 mortar:	roughly equivalent to Clashach sandstone

The porosity of these mortars and sandstones is:

mortar	(%)	**sandstone**	(%)
lime:	29	Locharbriggs:	24
1:3:12:	31	Stainton:	18
1:1:6:	27	Clashach:	16

These results show that the effects of porosity in mortar and sandstone differ with respect to depth of penetration of water repellents.

Mortar mix	Panel No.	Treatment	Porosity (%)		Exterior-interior porosity (%)
			External (treated)	Internal (untreated)	
lime	1	untreated control	31.4	33.5	-2.1
lime	2	untreated control	24.8	30.7	-2.7
lime	2	Con. A (var. 2)	27.5	31.5	-4.0
lime	2	Con. B	30.0	30.4	-0.4
lime	1	Water Rep./Con. C	25.6	28.7	-3.1
lime	1	Water Rep. D	31.6	21.9	14.2
1:3:12	3	untreated control	28.7	31.9	-3.2
1:3:12	4	untreated control	30.7	31.0	-0.4
1:3:12	4	Con. A (var. 2)	30.7	34.4	-3.7
1:3:12	4	Con. B	28.4	31.0	-2.6
1:3:12	3	Water Rep./Con. C	21.1	30.7	-9.6
1:3:12	3	Water Rep. D	26.4	29.5	-5.3
1:1:6	5	untreated control	31.0	23.6	7.3
1:1:6	6	untreated control	28.0	30.1	-2.1
1:1:6	6	Con. A (var. 1)	25.3	29.4	-4.1
1:1:6	6	Con. B	26.9	30.0	-3.2
1:1:6	5	Water Rep./Con. C	21.2	26.7	-5.5
1:1:6	5	Water Rep. D	23.2	18.7	4.5

Table 22 Total effective porosity in mortar core samples.

Treatment	Mortar	Mode of PSD of treated mortar (μm)	Mode of PSD of untreated mortar (μm)	Is pore diameter reduced on treated mortar?
None	Lime	2.9	3.3	yes
	Lime	3.3	3.3	no
	1:3:12	0.7	1.1	yes
	1:3:12	0.7	1.1	yes
	1:1:6	0.4	0.5	yes
	1:1:6	1.1	1.3	yes
Consolidant A	Lime	2.9	3.3	yes
	1:3:12	1.0	1.0	no
	1:1:6	0.9	1.1	yes
Consolidant B	Lime	3.9	2.9	no
	1:3:12	0.8	1.0	yes
	1:1:6	0.9	1.3	yes
Water Rep/Con C	Lime	2.9	3.3	yes
	1:3:12	0.7	1.3	yes
	1:1:6	0.6	0.7	yes
Water Rep. D	Lime	3.9	7.4	yes
	1:3:12	1.8	0.7	no
	1:1:6	0.4	0.4	yes

Table 23 Change in pore size distribution between treated (external) and untreated (internal) mortar samples from test panels. (PSD: pore size distribution)

Size range (μm)	**Change in porosity on treatment (%)**				
Lime mortar	**None**	**Con. A**	**Con. B**	**Water Rep/Con C**	**Water Rep. D**
1000 - 100	-4.3	0.6	2.7	2.6	3.7
100 - 10	-2.6	-0.1	1.1	-4.3	-0.9
10 - 1	-3.8	-18.8	1.7	-17.6	10.5
1 - 0.1	-3.1	3.1	0.1	4.0	20.4
0.1 - 0.01	0.7	1.9	-6.1	2.2	7.2
0.01 - 0.001	0.0	1.1	-0.6	1.6	0.4
1:3:12 mortar					
1000 - 100	4.7	-30.2	1.7	0.3	-4.3
100 - 10	0.4	0.3	-0.4	0.8	-0.1
10 - 1	-9.0	-9.6	-12.3	-17.7	25.8
1 - 0.1	5.3	20.8	7.9	2.5	-18.4
0.1 - 0.01	-6.9	7.1	-3.5	-16.5	-13.0
0.01 - 0.001	-1.0	0.3	-2.2	-1.4	-1.1
1:1:6 mortar					
1000 - 100	4.7	0.1	-1.4	-3.9	-5.3
100 - 10	-0.9	-0.5	-0.2	-5.7	2.3
10 - 1	9.6	-11.0	-4.3	-4.2	-8.8
1 - 0.1	-3.8	7.6	4.7	-1.7	34.5
0.1 - 0.01	0.6	-8.6	-7.6	-3.7	2.9
0.01 - 0.001	0.2	-2.1	-1.9	-0.3	-0.3

Table 24 Change in percentage of porosity within particular pore size ranges (see Table 18 for explanation of calculation). Data shown graphically in Figure 23.

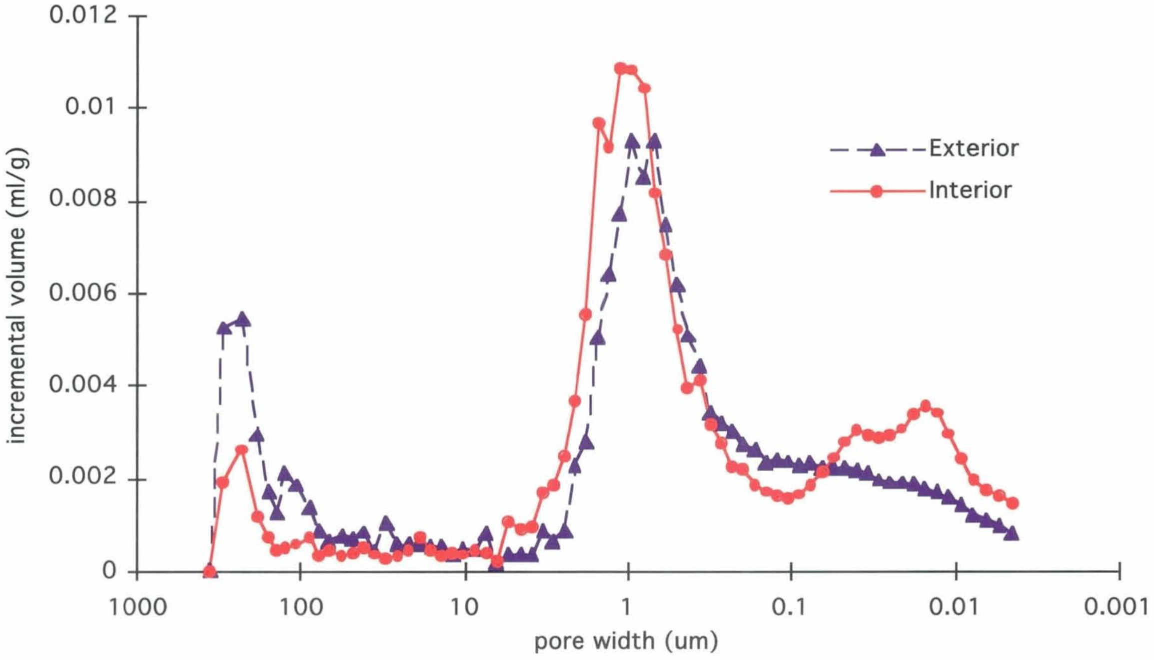


Figure 54a Mercury porosimetry of 1:3:12 mix mortar control.

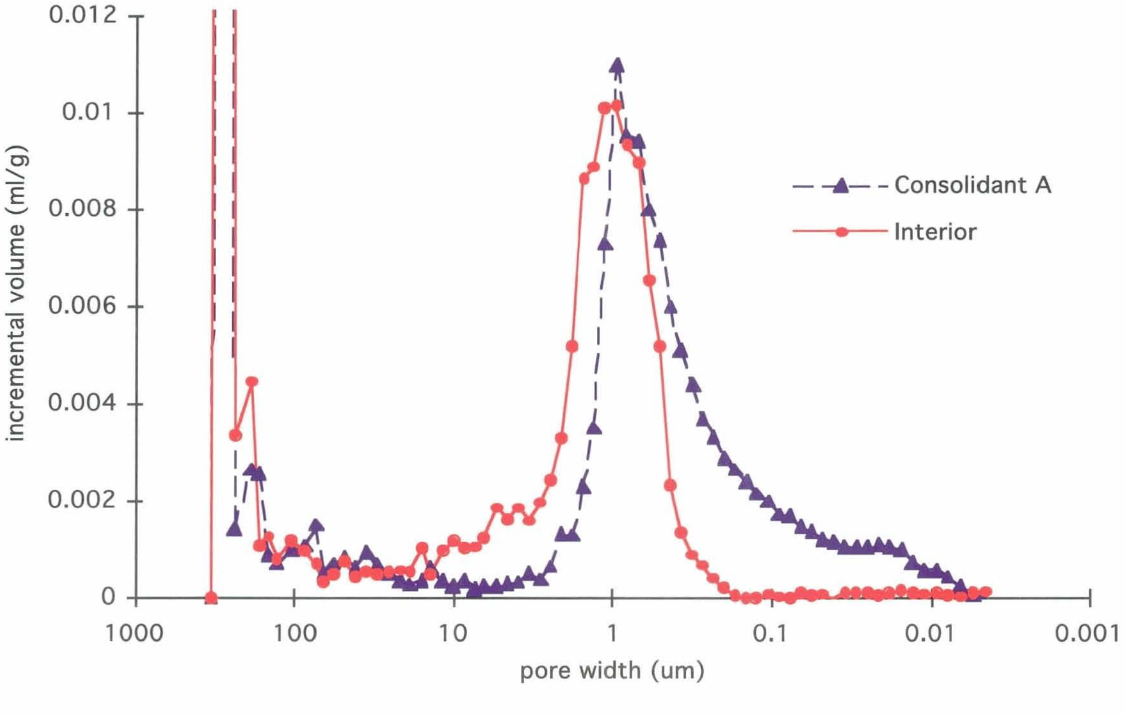


Figure 54b Mercury porosimetry of 1:3:12 mix mortar treated with Consolidant A (variety 2).

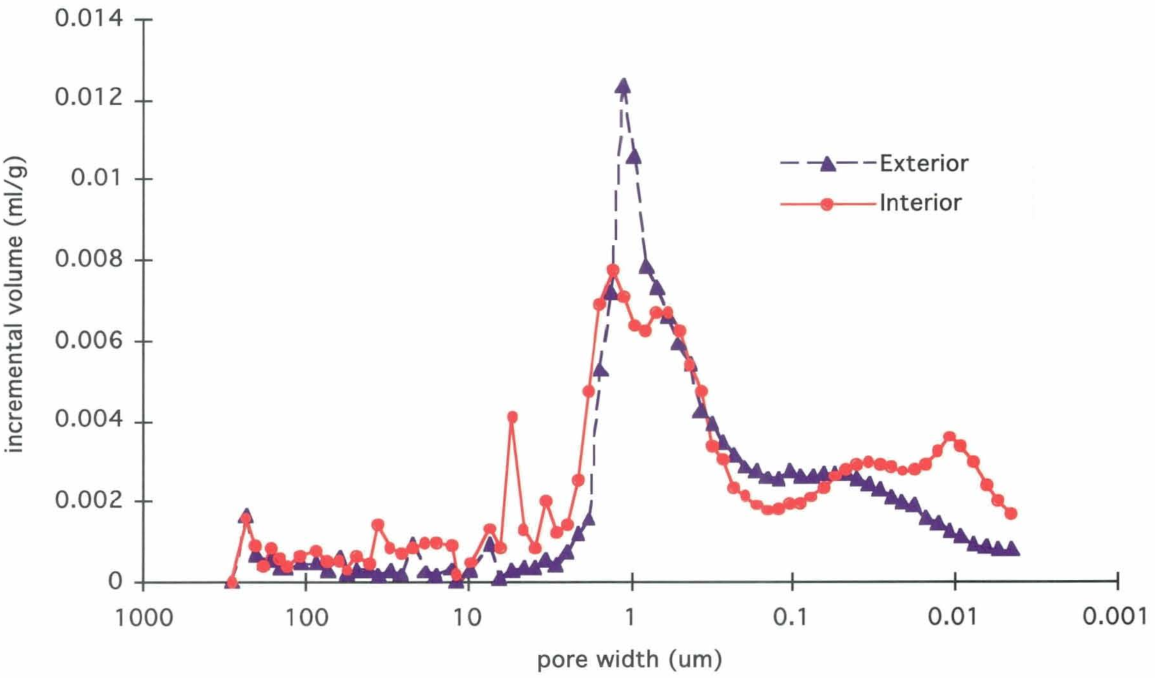


Figure 54c Mercury porosimetry of 1:1:6 mix mortar control.

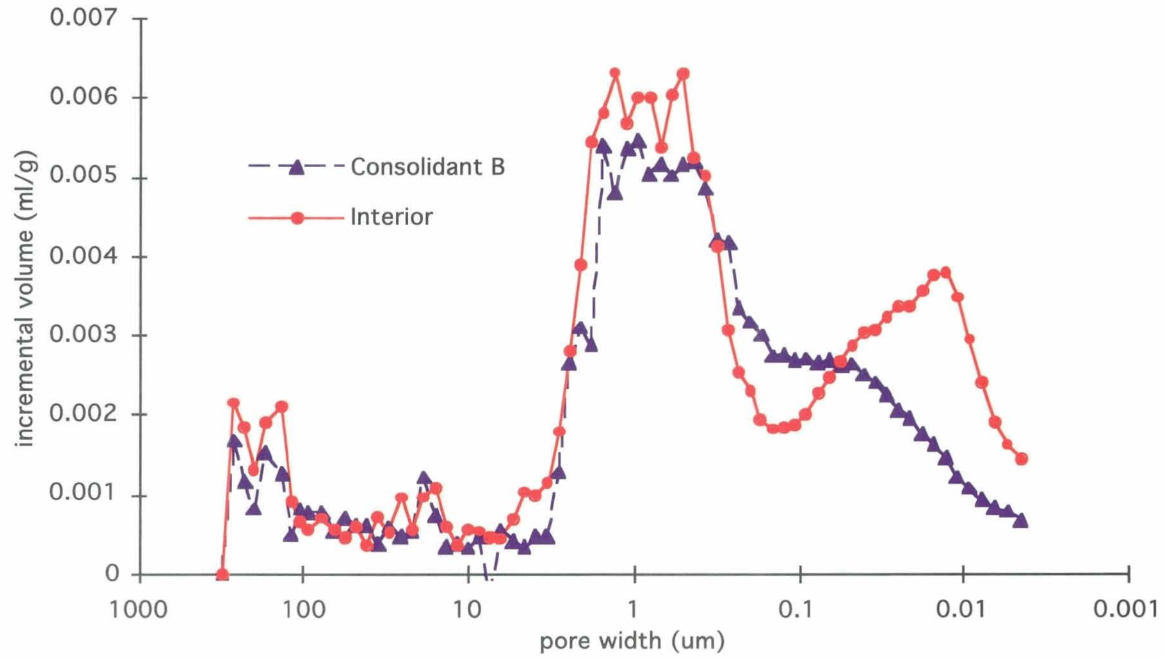


Figure 54d Mercury porosimetry of 1:1:6 mix mortar treated with Consolidant B.

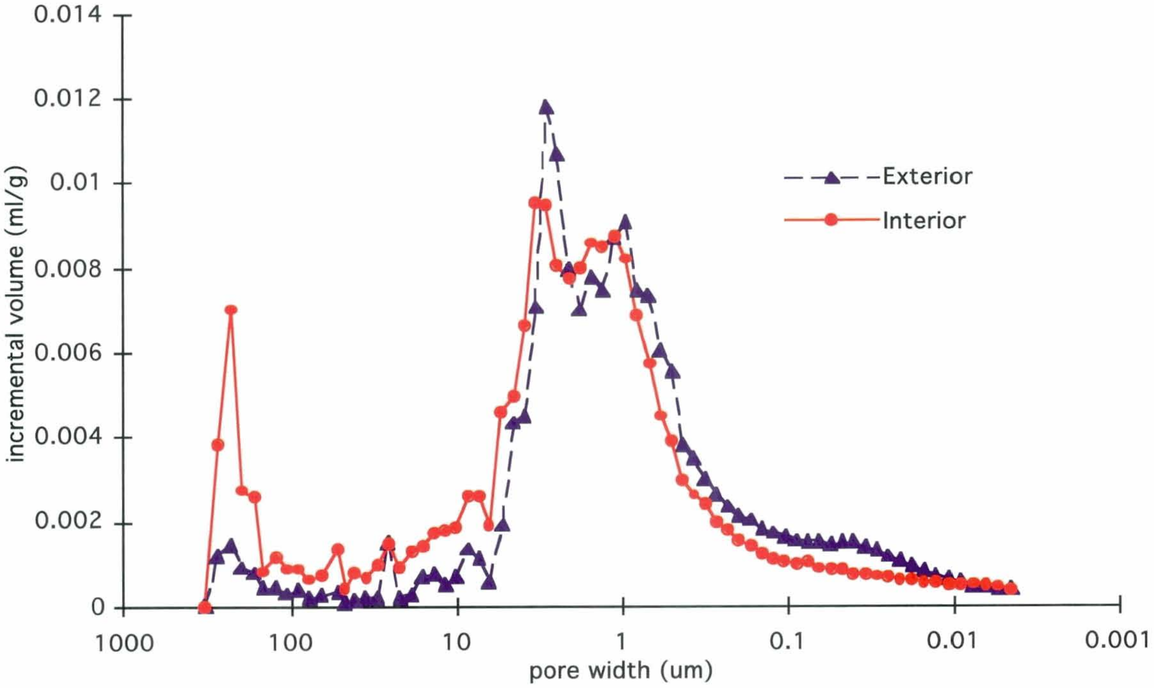


Figure 54e Mercury porosimetry of lime mortar control (untreated).

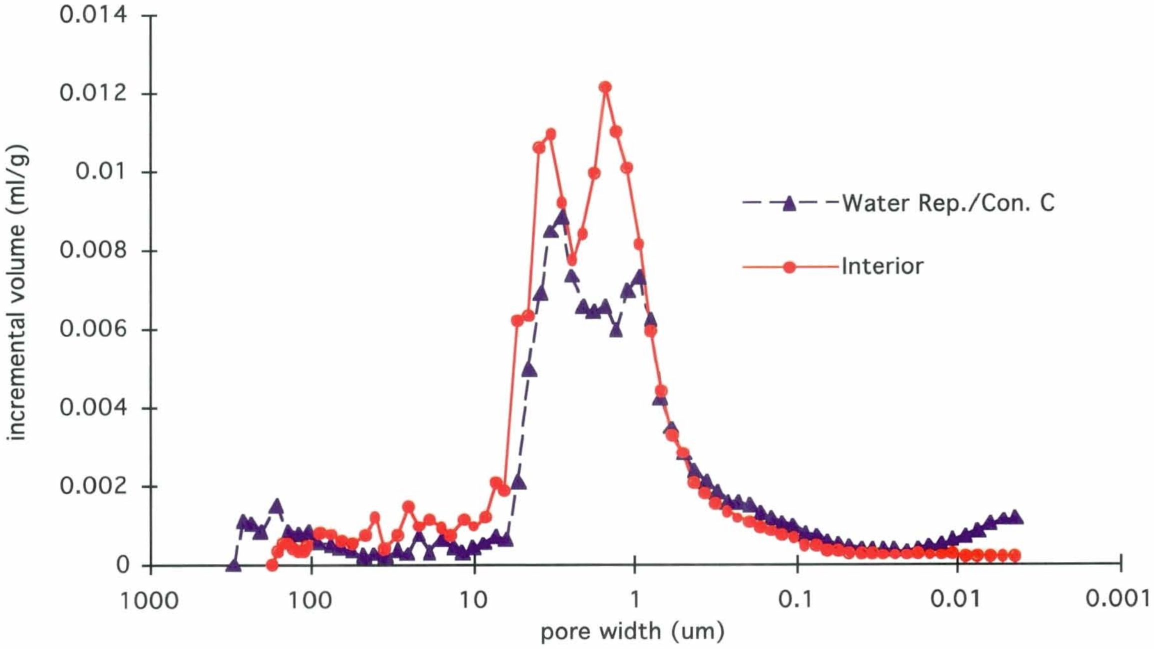


Figure 54f Mercury porosimetry of lime mortar treated with Water Rep./Con. C.

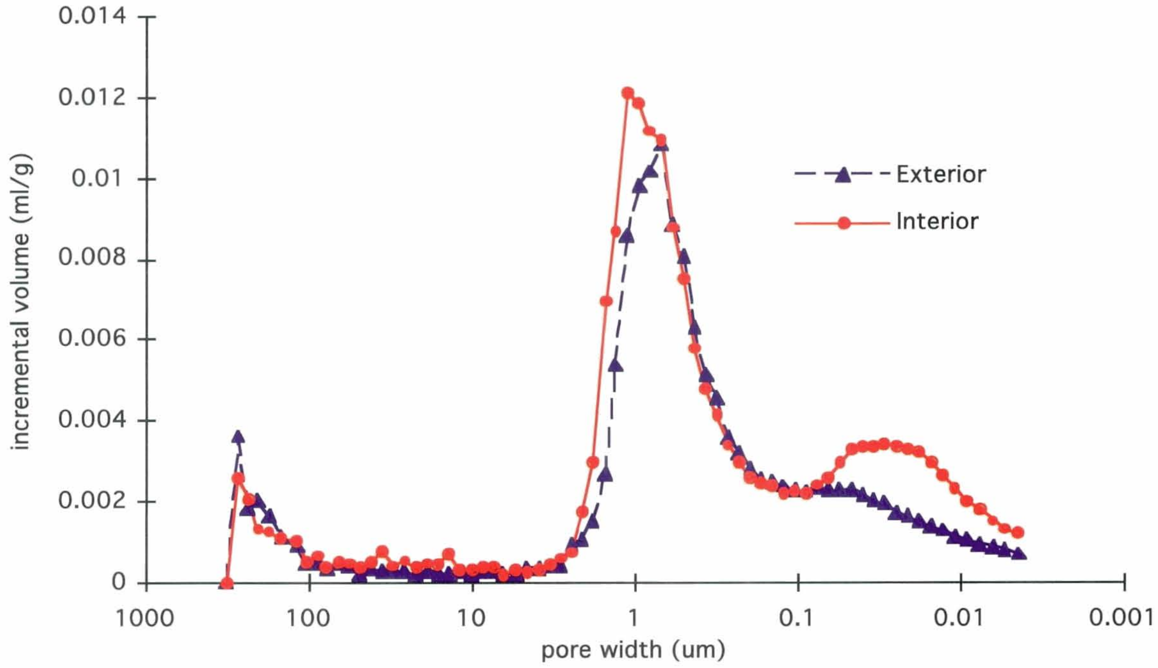


Figure 54g Mercury porosimetry of 1:3:12 mortar control (untreated).

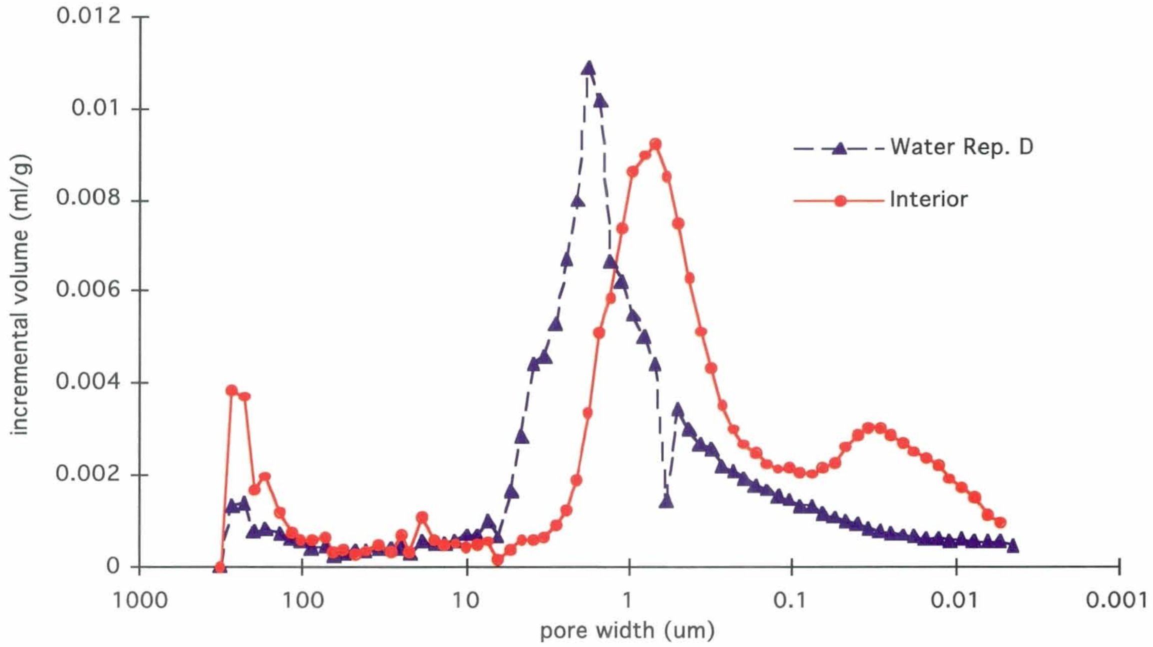


Figure 54h Mercury porosimetry of 1:3:12 mortar treated with Water Repellent D.

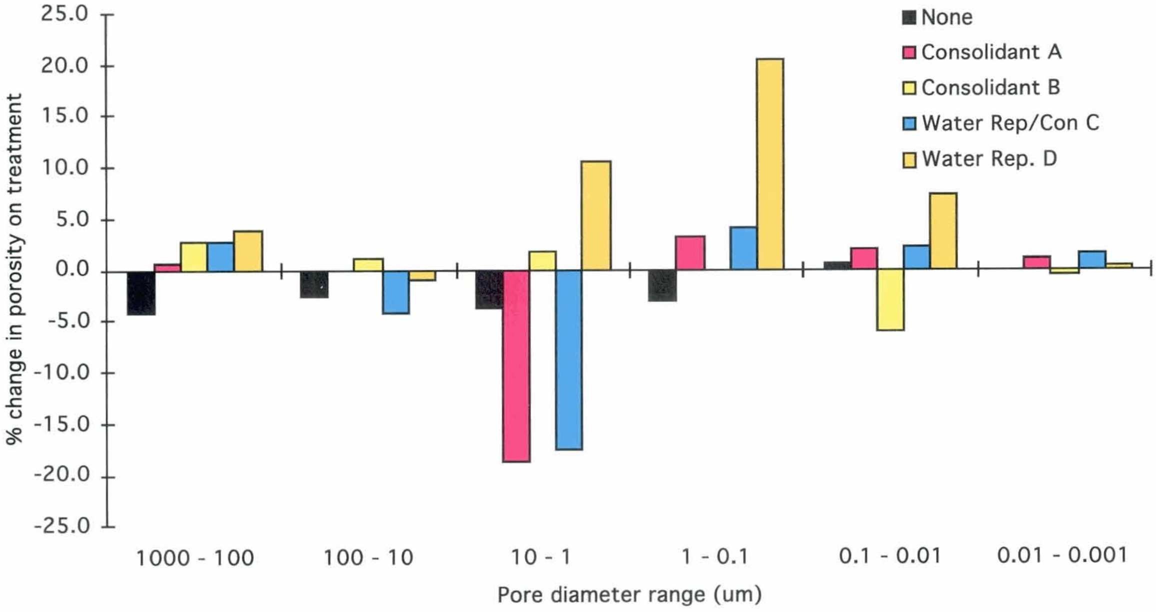


Figure 55a *Lime mortar. Change in percentage of porosity within particular pore size ranges. Data from Table 4.21.*

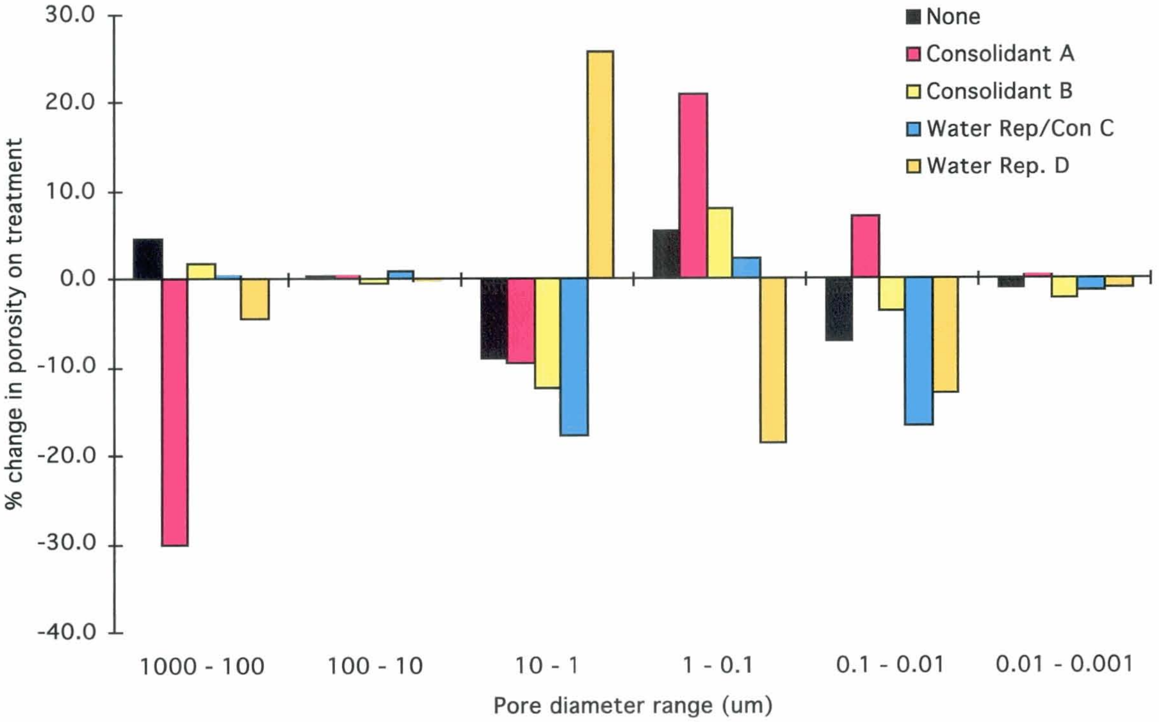


Figure 55b *1:3:12 mortar. Change in percentage of porosity within particular pore size ranges. Data from Table 4.21.*

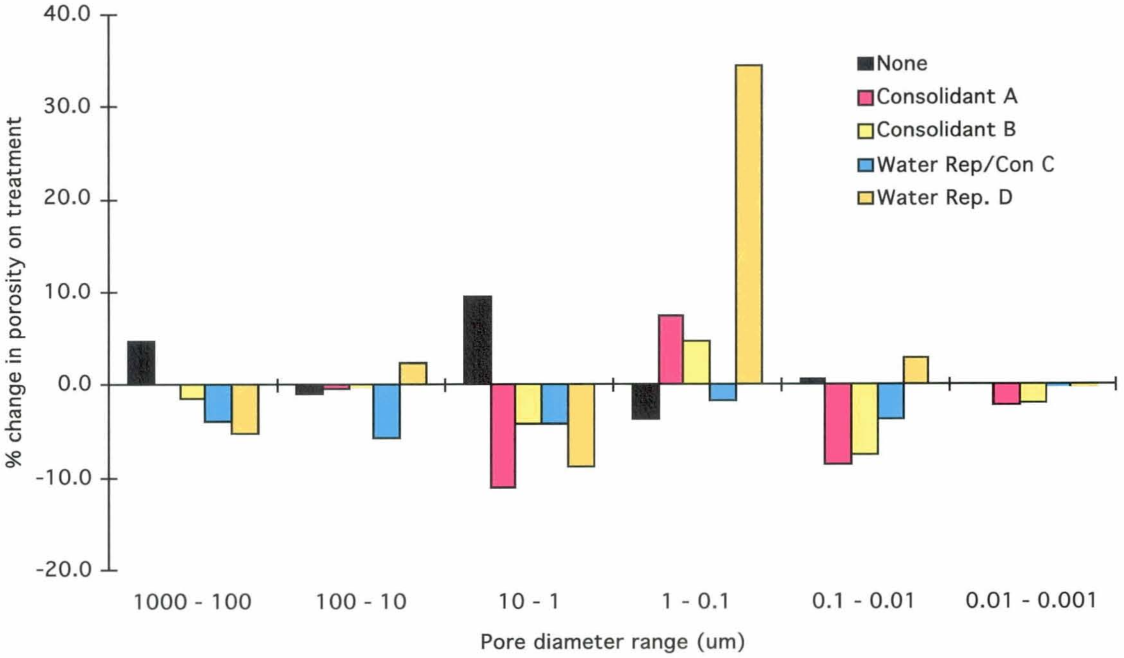


Figure 55c 1:1:6 mortar. Change in percentage of porosity within particular pore size ranges. Data from Table 24.

4.6 Effects of chemical cleaning on consolidant and water repellent treated sandstones

Samples of soiled and fresh Locharbriggs, Clashach and Leoch sandstones were selected for this experiment. The fresh Locharbriggs and Clashach sandstones were provided, freshly cut, by Locharbriggs and Clashach quarries. Fresh surfaces of Leoch sandstone were obtained by sawing large blocks of soiled Leoch sandstone. In each case the 'fresh' face was at least 150 mm below the original soiled surface. Soiled Locharbriggs, Clashach and Leoch sandstones were obtained from building demolitions. Their history and previous locations are not known.

Suitable samples (Figure 56) were cut and their colour and water repellency prior to treatment was measured. Separate samples of each were then treated with a consolidant (Water Rep./Con. C) and a water repellent (Water Repellent D). After allowing the samples 2 months to mature, their colour and water repellency were measured again and samples were subjected to chemical stonecleaning. The chemicals used were Neolith products commonly used for cleaning building facades (Neolith HDL and Neolith 625SS). The treatment regime was:

- Pre-wet the stone using high pressure water lance.
- Apply Neolith HDL according to the manufacturers' specifications.
- Leave the Neolith HDL on the stone for a dwell time of 20 minutes.
- Wash off Neolith HDL with high pressure water lance for 5 minutes.
- Apply Neolith 625SS according to the manufacturers' specifications.
- Leave Neolith 625SS on the stone for a dwell time of 5 minutes.
- Wash off Neolith 625SS with high pressure water lance for 5 minutes.

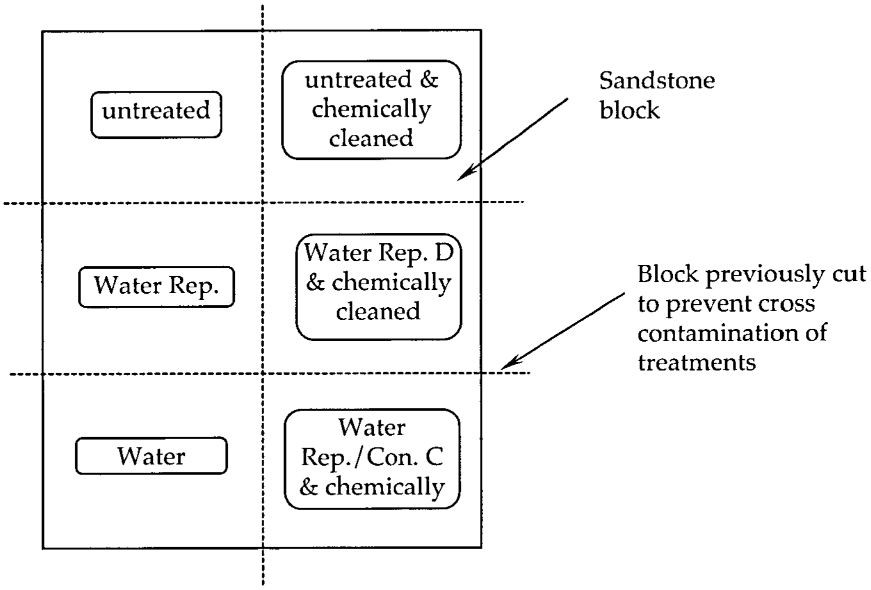


Figure 56 Plan for treatment and cleaning of sandstone blocks.

Following chemical cleaning the colour of the samples was re-measured. Depth drilling samples were taken from 0-2mm, 2-5mm, 5-10mm, 10-15mm and 15-20mm depths in the samples for the assessment of soluble salt distribution. Soluble materials in the sandstones will include naturally occurring soluble salts, residues of atmospheric pollutants and residues of the chemical cleaning agents.

4.6.1 Colour changes following treatment

The colour of the sandstone blocks was measured (by chroma meter) before treatment, after treatment (Water Repellent D or Water Rep./Con. C) and after chemical cleaning. Control blocks, untreated and/or uncleaned were also colour measured at the same intervals. A summary table of colour change data is shown in Table 25. Selected graphical data on colour changes are shown in Figure 57. These data show colour changes attributable either to water repellent/consolidants treatment and to chemical cleaning.

Some relatively minor colour changes occurred on the control, untreated, uncleaned sandstone (Figure 57) which are attributable to soiling during storage or cutting of samples. Larger colour changes can be seen to be caused by water repellent/consolidant treatments and cleaning (Table 25).

Both the Water Repellent D and Water Rep./Con. C treatments caused similar colour changes resulting in darkening of the sandstone (mean -7%, range -3% to -11%) and increased red and yellow coloration (mean +2, ranges: red 0 to +5, yellow 0 to +6). Cleaning of the (untreated) samples also caused colour changes resulting, on average, in a 3% fall in lightness (range -6% to 0%) and 3% increases in red and yellow coloration (ranges: red 0 to +8, yellow -1 to +10). Cleaning of sandstones previously treated with water repellent or consolidant resulted in lightening of the previously darkened surfaces (mean +3%, range -4% to +12%) and further increased red (mean +2, range -1 to +6) and yellow (mean +1, range -4 to +8) coloration.

The treatments did not appear to interfere with soiling removal from the sandstone surfaces. In addition, the lightness losses on treatment with water repellents/consolidants were reversed on chemical cleaning although the final lightness of treated surfaces often remained darker than that of untreated surfaces (especially where the sandstones were initially soiled). While the water repellent/consolidant treatments could cause some colour changes, much greater degrees of colour change were caused by chemical cleaning especially on highly coloured, initially soiled sandstone types.

In summary, the effects of water repellent/consolidant treatment were mainly to cause darkening of the sandstones (Table 26). There was a relatively minor effect on colour (slight reddening and yellowing). Chemical cleaning, especially of highly coloured, soiled sandstones caused more intense reddening and yellowing. Chemical cleaning also caused darkening of sandstones, especially where these were initially unsoiled. The degree of lightness change on the soiled samples measured here was relatively slight, ranging from slight lightening to slight darkening. The degree of lightness change on soiled sandstones will obviously depend strongly on the degree of pre-existing soiling.

Sandstone	Soiled /fresh	Treatment	L*			a*			b*		
			B	T	C	B	T	C	B	T	C
Locharbriggs	soiled	Water Rep./Con. C	39	30	41	5	6	11	11	11	15
		Water Rep. D	39	32	39	4	5	11	10	11	16
		none	45	45	45	4	7	12	12	13	17
Clashach	soiled	Water Rep./Con. C	53	45	53	0	5	8	17	21	25
		Water Rep. D	51	46	48	1	3	8	15	18	26
		none	52	51	50	0	2	7	14	15	24
Leoch	soiled	Water Rep./Con. C	47	40	43	-1	0	2	9	10	8
		Water Rep. D	46	43	42	0	0	1	8	9	7
		none	44	45	41	0	-1	-1	7	7	6
Locharbriggs	fresh	Water Rep./Con. C	51	41	48	10	12	11	15	16	15
		Water Rep. D	49	44	48	11	12	12	16	17	17
		none	48	48	44	12	12	14	16	16	18
Clashach	fresh	Water Rep./Con. C	65	56	61	2	4	3	12	18	14
		Water Rep. D	66	54	58	2	4	4	13	19	17
		none	63	63	58	3	3	4	15	15	18
Leoch	fresh	Water Rep./Con. C	62	52	50	0	0	0	7	8	6
		Water Rep. D	59	56	52	0	0	1	7	7	6
		none	54	51	48	-1	-1	-1	5	6	5

L*: lightness (higher value = lighter)

a*: red-green colour (+ve values = redder)

b*: blue-yellow colour (+ve values = yellower)

B: before treatment

T: after Water Rep./Con. C or Water Repellent D treatment

C: after Water Rep./Con. C or Water Repellent D treatment and chemical cleaning

Table 25 Measured lightness and colour values of treated, chemically cleaned sandstones.

Treatment type	Mean colour change		
	L*	a*	b*
Water Repellent D	-5	1	2
Water Rep/Con. C	-9	2	2
Water Rep. D & chemical cleaning	-4	3	3
Water Rep/Con. C & chemical cleaning	-3	3	2
Chemical cleaning	-3	3	3

Table 26 Summary table, for all sandstone types, of colour changes from before treatment.

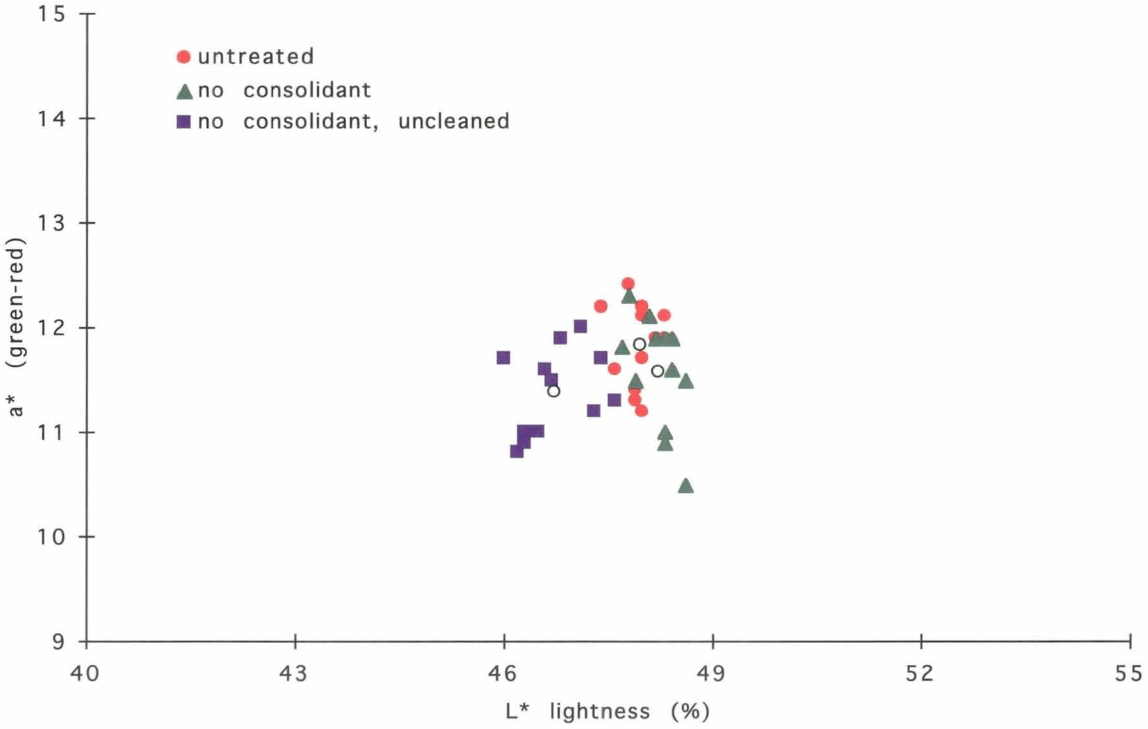


Figure 57a *Colour changes measured on sandstone blocks which have undergone treatment with water repellents/consolidants and chemical cleaning. Untreated, uncleaned block of fresh Locharbriggs sandstone*

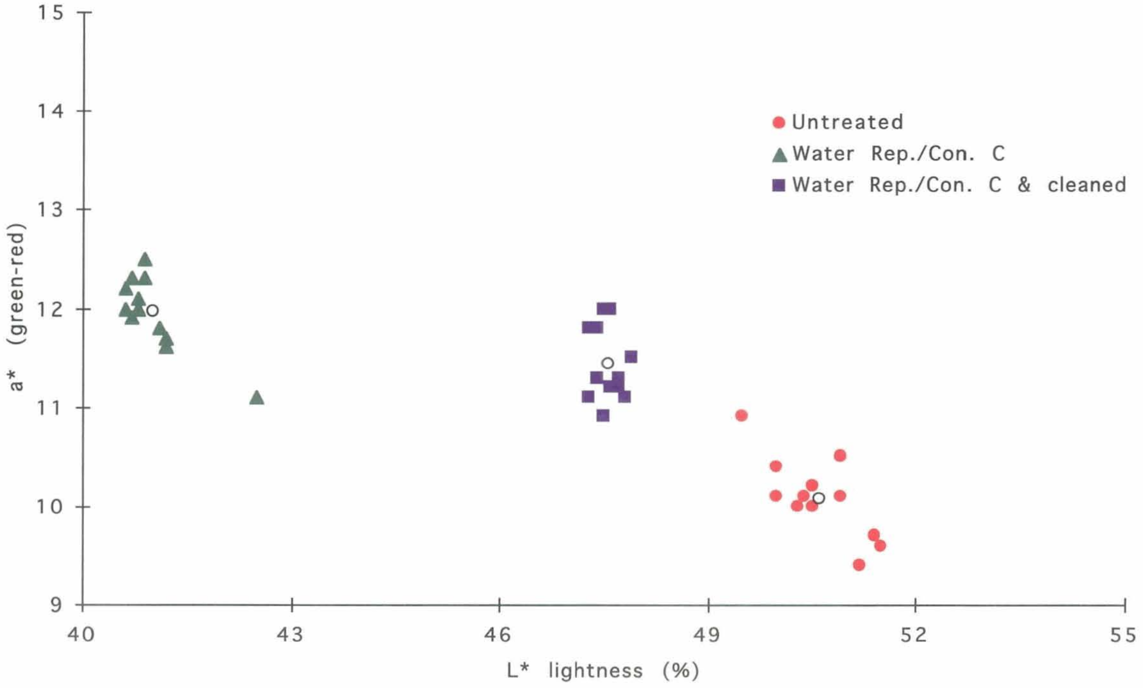


Figure 57b *Colour changes measured on sandstone blocks which have undergone treatment with water repellents/consolidants and chemical cleaning. Fresh Locharbriggs sandstone after treatment with Water Repellent/Consolidant C and chemical cleaning.*

4.6.2 Results of depth profiling for chemical residues

The results from depth profiling of treated and untreated, soiled and fresh Locharbriggs, Clashach and Leoch sandstones are shown in Figure 58. This method measures the soluble salts present in the sandstone samples at various depths (0-2 mm, 2-5 mm, 5-10 mm, 10-15 mm & 15-20 mm).

Sodium

Soluble sodium in the samples could be derived at relatively low levels from naturally occurring minerals in the sandstone (e.g. feldspars), from pollutants passing into the stone through its surface (e.g. aerosols of sea spray or de-icing salts) or from residues of applied chemicals (e.g. alkaline cleaning agent).

For uncleaned samples, the amount of soluble sodium in fresh and soiled Locharbriggs and Clashach sandstones was generally relatively low (<100 ppm). There was little difference in the levels of soluble sodium in the fresh and soiled sandstone samples indicating that sodium salts were not a significant component of the soiling of these sandstones. In fresh and soiled Leoch sandstone the amounts in the untreated sandstone were higher (up to approx. 1000 ppm) due to the larger amount of sodium (approx. 2%) in this sandstone compared to the others (<<1%). Occasional, sudden variations in sodium content with depth are likely to be due to the presence of more sodium rich minerals at that location. Soiled Leoch sandstone showed some evidence of relative depletion in sodium in the outer 2 mm compared to its level deeper in the sandstone. This is similar to the results obtained for sulphate and chloride levels indicating that in this stone type soluble salts may tend to become concentrated behind the outer surface of the stone.

There was no evidence that either of the treatments (Water Repellent D or Water Rep./Con. C) introduced any sodium into the treated sandstones.

Soluble sodium levels in most samples after cleaning were found to be elevated over levels in uncleaned samples. For the untreated stones, fresh and soiled Locharbriggs and Clashach sandstones showed substantially increased levels of sodium at up to 20 mm depth (the maximum depth of sampling). Results generally indicated that the highest sodium residues were present close to the surface of the sandstones, with levels declining as depth into the stone increased. This is the pattern that would be expected where the sodium has been introduced into the sandstone by application of a chemical to its surface. Untreated Leoch sandstone samples exhibited no increase in soluble sodium levels in the chemically cleaned relative to the uncleaned samples. As this sandstone has a very low porosity (approx. 7%) and permeability, it is likely that the applied chemicals remained close to the stone surface on application and were completely removed on wash-off.

Following cleaning, the treated (Water Repellent D and Water Rep./Con. C) fresh and soiled Locharbriggs and Clashach sandstone samples also showed elevated soluble sodium levels. However, levels in the outer 0-2 mm of the sandstones were often lower than were found for the untreated sandstone and elevated sodium levels were not found beyond about 5 mm depth. The treated and cleaned Leoch sandstone samples (fresh and soiled) showed no evidence of any increased soluble sodium levels beyond those in the control samples.

These results indicate that:

- Levels of soluble sodium in fresh sandstone may vary considerably depending on the sandstone composition.
- Levels of soluble sodium in the soiled sandstones were not significantly higher than in the fresh sandstones.
- The consolidant/water repellent treatments (Water Repellent D and Water Rep./Con. C) did not introduce any soluble sodium into the sandstones.
- Application of consolidants/water repellents had no immediate effect on the distribution of soluble sodium in soiled sandstones.
- Soluble sodium residues from chemical cleaning of porous sandstones could be found at up to 20 mm depth in untreated sandstone.
- Soluble sodium residues from chemical cleaning of treated (Water Repellent D and Water Rep./Con. C) porous sandstones were often lower than those found in untreated sandstones.
- Soluble sodium residues from chemical cleaning of treated (Water Repellent D and Water Rep./Con. C) porous sandstones remained relatively close to the surface, being found at up to 5 mm depth.

Fluoride

Naturally occurring levels of soluble fluoride in most sandstone is below the level of detection (here 10 ppm) and fluoride is not normally a component of atmospheric pollution. Therefore any soluble fluoride in these samples is likely to be a residue of applied chemicals (e.g. acid cleaning agent).

For uncleaned samples, the amount of soluble fluoride in fresh and soiled Locharbriggs and Clashach sandstones was generally below the level of detection (i.e. <10 ppm). In fresh and soiled Leoch sandstone the amounts in the untreated sandstone were higher (up to approx. 50 ppm) due to the larger amount of fluoride in this sandstone. There was no evidence that either of the treatments (Water Repellent D or Water Rep./Con. C) introduced any fluoride into the treated sandstones.

Soluble fluoride levels in most samples after cleaning were found to be substantially elevated over levels in uncleaned samples. For the untreated stones, fresh Locharbriggs and Clashach sandstones showed substantially increased levels of fluoride at up to 20 mm depth (the maximum depth of sampling), with results suggesting that further drilling would have found increased levels at greater depths. For the untreated, soiled Locharbriggs and Clashach sandstones, results also indicated increased levels of fluoride at up to 20 mm depth although the amount of fluoride showed a rather more rapid decline with depth than was observed for the fresh sandstone samples. Fresh and soiled, untreated Leoch sandstone also showed increased levels of soluble fluoride over those found in the uncleaned samples. Increased levels of soluble fluoride were found at up to 5 mm depth in fresh Leoch sandstone and at up to 10 mm depth in soiled Leoch sandstone. This contrasts with the results for depth profiling of sodium residues where no increased levels were found in Leoch sandstone.

Results for cleaned, untreated sandstones generally indicated that the highest soluble fluoride residues were present close to the surface of the sandstones, with levels declining as depth into the sandstone increased. This is the pattern which would be expected where the fluoride has been introduced into the sandstone by application of a chemical to its surface.

Following cleaning, the treated (Water Repellent D and Water Rep./Con. C) fresh and soiled Locharbriggs, Clashach and Leoch sandstone samples also showed elevated soluble fluoride levels, but these were generally confined to the outer 0-2 mm (occasionally 2-5 mm). Levels of soluble fluoride in the outer 0-2 mm of the sandstones were, in some cases, lower than were found for the untreated sandstone, but in other cases levels of soluble fluoride were comparable to, or greater than, levels in comparable untreated sandstone samples.

These results indicate that:

- Levels of soluble fluoride in fresh sandstone were generally very low but may be higher in some sandstone types (e.g. Leoch).
- Levels of soluble fluoride in the soiled sandstones were not significantly higher than in the fresh sandstones.
- The consolidant/water repellent treatments (Water Repellent D and Water Rep./Con. C) did not introduce any soluble fluoride into the sandstones.
- Application of consolidants/water repellents had no immediate effect on the distribution of soluble fluoride in soiled sandstones.
- Soluble fluoride residues from chemical cleaning of porous sandstones could be found at up to 20 mm depth in untreated sandstone.
- Soluble fluoride residues were higher in fresh porous sandstones than in soiled porous sandstones.
- Soluble fluoride residues from chemical cleaning of treated (Water Repellent D and Water Rep./Con. C) sandstones were often comparable to those found in untreated sandstones in the outer 0-2 mm, however,
- Soluble fluoride residues from chemical cleaning of treated (Water Repellent D and Water Rep./Con. C) sandstones remained relatively close to the surface being found at up to 2 mm (occasionally 5 mm) depth.

Phosphate

Soluble phosphate in the samples could be derived at relatively low levels from naturally occurring minerals in the sandstone (e.g. apatite), from pollutants passing into the stone through its surface (e.g. bird droppings) or from residues of applied chemicals (e.g. acid cleaning agent).

For uncleaned samples, the amount of soluble phosphate in fresh and soiled Locharbriggs, Clashach and Leoch sandstones was, in most cases, below the level of detection (<20 ppm). There was no difference in the levels of soluble phosphate in the fresh and soiled sandstone samples indicating that phosphate was not a significant component of the soiling of these sandstones. There was no evidence that either of the treatments (Water Repellent D or Water Rep./Con. C) introduced any phosphate into the treated sandstones.

Soluble phosphate levels in most samples after cleaning were found to be substantially elevated over levels in uncleaned samples. For the untreated stones, fresh and soiled Locharbriggs and Clashach sandstones showed increased levels of phosphate down to about 15-20 mm depth (the maximum depth of sampling). The highest phosphate residues were present close to the surface of the sandstones, with levels declining as depth into the stone increased. This is the pattern that would be expected where the phosphate has been introduced into the sandstone by application of a chemical to its surface. Untreated fresh Leoch sandstone exhibited no increase in soluble phosphate levels in the chemically cleaned relative to the uncleaned stone and soiled Leoch sandstone showed only a slight increase in soluble phosphate in the outer 2 mm. As this sandstone has a very low porosity (approx. 7%) and permeability, it is likely that the applied chemicals remained close to the stone surface on application and were completely removed on wash-off.

Following cleaning, the treated (Water Repellent D and Water Rep./Con. C) fresh and soiled Locharbriggs and Clashach sandstone samples also showed elevated soluble phosphate levels. However, levels in the outer 0-2 mm of the sandstones were often substantially lower than were found for the untreated sandstone and elevated phosphate levels were not found beyond about 2-5 mm depth. The treated and cleaned Leoch sandstone samples (fresh and soiled) showed slightly increased soluble phosphate levels at 0-2 mm depth with no detectable phosphate beyond that depth.

These results indicate that:

- Levels of soluble phosphate in fresh and soiled sandstone were low (generally <20 ppm).
- The consolidant/water repellent treatments (Water Repellent D and Water Rep./Con. C) did not introduce any soluble phosphate into the sandstones.
- Application of consolidants/water repellents had no immediate effect on the distribution of soluble phosphate in soiled sandstones.
- Soluble phosphate residues from chemical cleaning of porous sandstones could be found at up to 15-20 mm depth in untreated sandstone.
- Soluble phosphate residues from chemical cleaning of treated (Water Repellent D and Water Rep./Con. C) porous sandstones were often lower than those found in untreated sandstones.
- Soluble phosphate residues from chemical cleaning of treated (Water Repellent D and Water Rep./Con. C) porous sandstones remained relatively close to the surface seldom being found beyond 2 mm depth.

Sulphate

Soluble sulphate in the samples will be mainly derived from sulphur-bearing pollutants passing into the stone through its surface (e.g. SO_2 or aerosols) although some may be present naturally in the sandstone at a low level. Soluble sulphate should not be present either in the stonecleaning chemicals or in the consolidants/water repellents.

For uncleaned samples, the amount of soluble sulphate in fresh Locharbriggs, Clashach and Leoch sandstones was generally relatively low (<50 ppm for Locharbriggs and Clashach and <200 ppm for Leoch). The amounts found in uncleaned soiled Locharbriggs, Clashach and Leoch varied quite widely (from <50 ppm to >4000 ppm) indicating that sulphate was present in the soiling layer although its distribution was uneven. There was little evidence of any sulphates in the soiled Locharbriggs sandstone, soiled Clashach sandstone showed a 'typical' pattern of enrichment in sulphate close to the stone surface with levels declining with increasing depth into the stone, approaching background levels by about 20 mm depth. In the soiled Leoch sandstone sulphate levels were low in the outer 2 mm but high from 2-10 mm depth indicating that in this stone type soluble salts may tend to become concentrated behind the outer surface of the stone. Similar, but less pronounced, indications of this were noted in the data for sodium and chloride depth profiling in soiled Leoch sandstone. In both these cases there was a tendency for the soluble ions to be more concentrated below the outer 2 mm of the stone.

There was no evidence that either of the treatments (Water Repellent D or Water Rep./Con. C) introduced any sulphate into the treated sandstones.

Soluble sulphate levels in treated and untreated, fresh and soiled Locharbriggs, Clashach and Leoch samples after cleaning were found to be very similar to those before cleaning indicating that chemical cleaning did not introduce sulphate into the samples, nor did it removed any appreciable amount from the soiled sandstones.

These results indicate that:

- Levels of soluble sulphate were low in fresh sandstone.
- Levels of soluble sulphate in soiled sandstone, derived from deposition of pollutants, may vary widely between samples and can also show considerable variation across a single sample.
- Soluble sulphate levels were not necessarily highest near the outer surface of soiled sandstone, in some cases they may be more concentrated several millimetres into the stone.
- The consolidant/water repellent treatments (Water Repellent D and Water Rep./Con. C) did not introduce any soluble sulphate into the sandstones.
- Application of consolidants/water repellents had no immediate effect on the distribution of soluble sulphate in soiled sandstones.
- No soluble sulphate was introduced into the sandstones by chemical cleaning.

Chloride

Soluble chloride in the samples will be mainly derived from chlorine-bearing pollutants passing into the stone through its surface from aerosols in coastal environments or from de-icing salts spread on roads and pavements. Some chloride may be present naturally in the sandstone at a relatively low level. Soluble chloride should not be present either in the stonecleaning chemicals or in the consolidants/water repellents.

For uncleaned samples, the amount of soluble chloride in fresh Locharbriggs, Clashach and Leoch sandstones was generally relatively low (<200 ppm). The amounts found in uncleaned soiled Locharbriggs, Clashach and Leoch were similar to those in fresh sandstone (<200 ppm) indicating that chloride was not a significant component of the soiling layer. There was no evidence of any concentration of soluble chloride towards the outer surface of the sandstones. Soiled Leoch sandstone showed some evidence of relative depletion in chloride in the outer 2 mm compared to its level deeper in the sandstone. This is similar to the results obtained for sulphate and sodium levels indicating that in this stone type soluble salts may tend to become concentrated behind the outer surface of the stone.

There was no evidence that either of the treatments (Water Repellent D or Water Rep./Con. C) introduced any chloride into the treated sandstones.

Soluble chloride levels in treated and untreated, fresh and soiled Locharbriggs, Clashach and Leoch samples after cleaning were found to be very similar to those before cleaning indicating that chemical cleaning did not introduce chloride into the samples, nor did it removed any appreciable amount from the soiled sandstones.

These results indicate that:

- Levels of soluble chloride were low in fresh and soiled sandstones.
- Soluble chloride levels showed no tendency to be concentrated near the outer surface of soiled sandstone.
- The consolidant/water repellent treatments (Water Repellent D and Water Rep./Con. C) did not introduce any soluble chloride into the sandstones.
- Application of consolidants/water repellents had no immediate effect on the distribution of soluble chloride in soiled sandstones.
- No soluble chloride was introduced into the sandstones by chemical cleaning.

Nitrate

Soluble nitrate in the samples may be derived from nitrate-bearing pollutants passing into the stone through its surface (e.g. from bird droppings). Nitrate may also be derived from the action of some nitrogen-fixing bacteria.

Soluble nitrate should not be present either in the stonecleaning chemicals or in the consolidants/water repellents.

For uncleaned samples, the amount of soluble nitrate in fresh Locharbriggs and Clashach sandstones was generally relatively low (from below the limit of detection (20 ppm) to approx. 100 ppm). The amounts found in uncleaned soiled Locharbriggs and Clashach sandstone were, in some cases, slightly higher than those in fresh sandstone (up to approx. 300 ppm). While higher nitrate values tended to occur close to the sandstone surface, there was no evidence of any overall pattern in concentration suggesting a regular decline in concentration with depth. Both fresh and soiled Leoch sandstone occasionally had relatively higher nitrate levels than were found in the other sandstone types (<850 ppm) although some samples had nitrate levels close to the limit of detection (20 ppm). The higher nitrate levels in the freshly cut Leoch sandstone occurred mainly in the outer 2 mm. Since this sandstone was freshly cut prior to its use in this experiment, it is unlikely that this could represent natural contamination. It is possible that the nitrate was derived from contamination during sample cutting or handling. The fact that the fresh Leoch sandstone samples generally had higher levels of soluble nitrate than soiled Leoch sandstone would tend to support this possibility. Occasional peaks in nitrate, such as occurred in fresh Locharbriggs sandstone, may be due to unusual concentrations of soluble nitrate present in the sandstone or to some other contamination of the sample.

There was no evidence that either of the treatments (Water Repellent D or Water Rep./Con. C) introduced any nitrate into the treated sandstones.

Soluble nitrate levels in treated and untreated, fresh and soiled Locharbriggs, Clashach and Leoch samples after cleaning were found to be very similar to those before cleaning indicating that chemical cleaning did not introduce nitrate into the samples.

These results indicate that:

- Levels of soluble nitrate were generally low in fresh and soiled sandstones.
- Soluble nitrate levels showed some tendency to be concentrated near the outer surface of soiled sandstone although their interior distribution showed little consistency.
- The consolidant/water repellent treatments (Water Repellent D and Water Rep./Con. C) did not introduce any soluble nitrate into the sandstones.
- Application of consolidants/water repellents had no immediate effect on the distribution of soluble nitrate in soiled sandstones.
- No soluble nitrate was introduced into the sandstones by chemical cleaning.

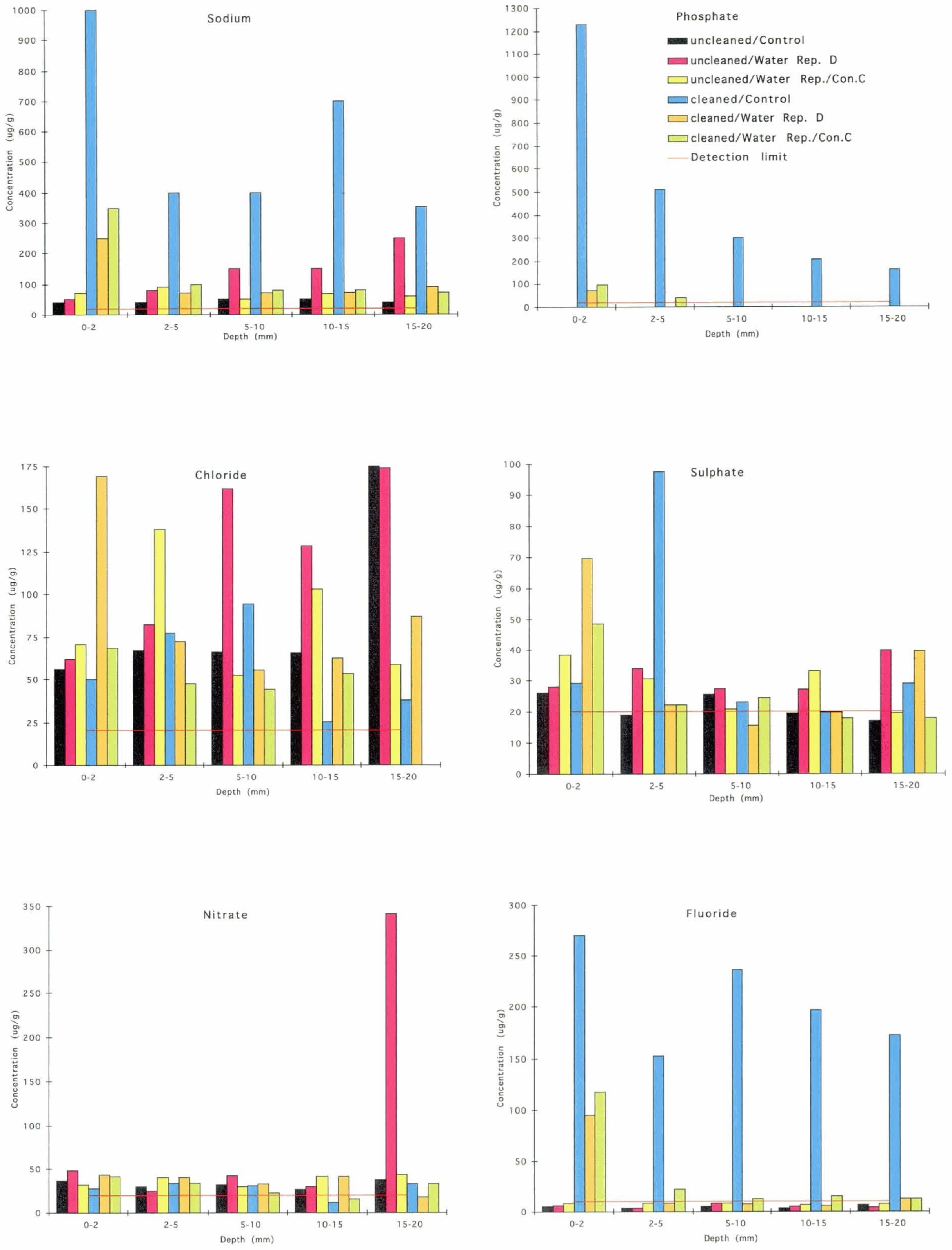


Figure 58a ***Fresh Locharbriggs sandstone****. Soluble ions in treated or untreated blocks of sandstone before and after chemical cleaning.*

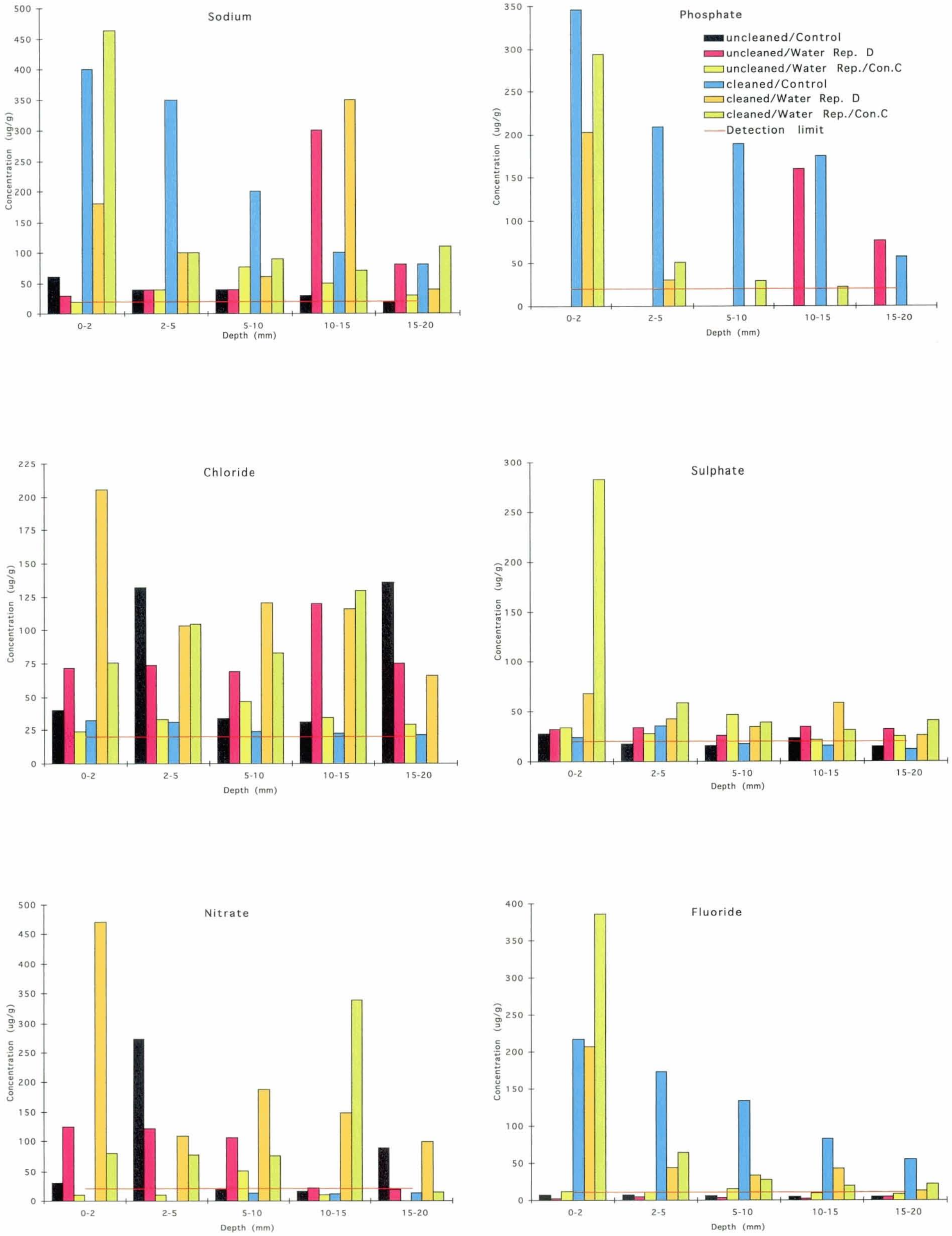


Figure 58b ***Soiled Locharbriggs sandstone.*** *Soluble ions in treated or untreated blocks of sandstone before and after chemical cleaning.*

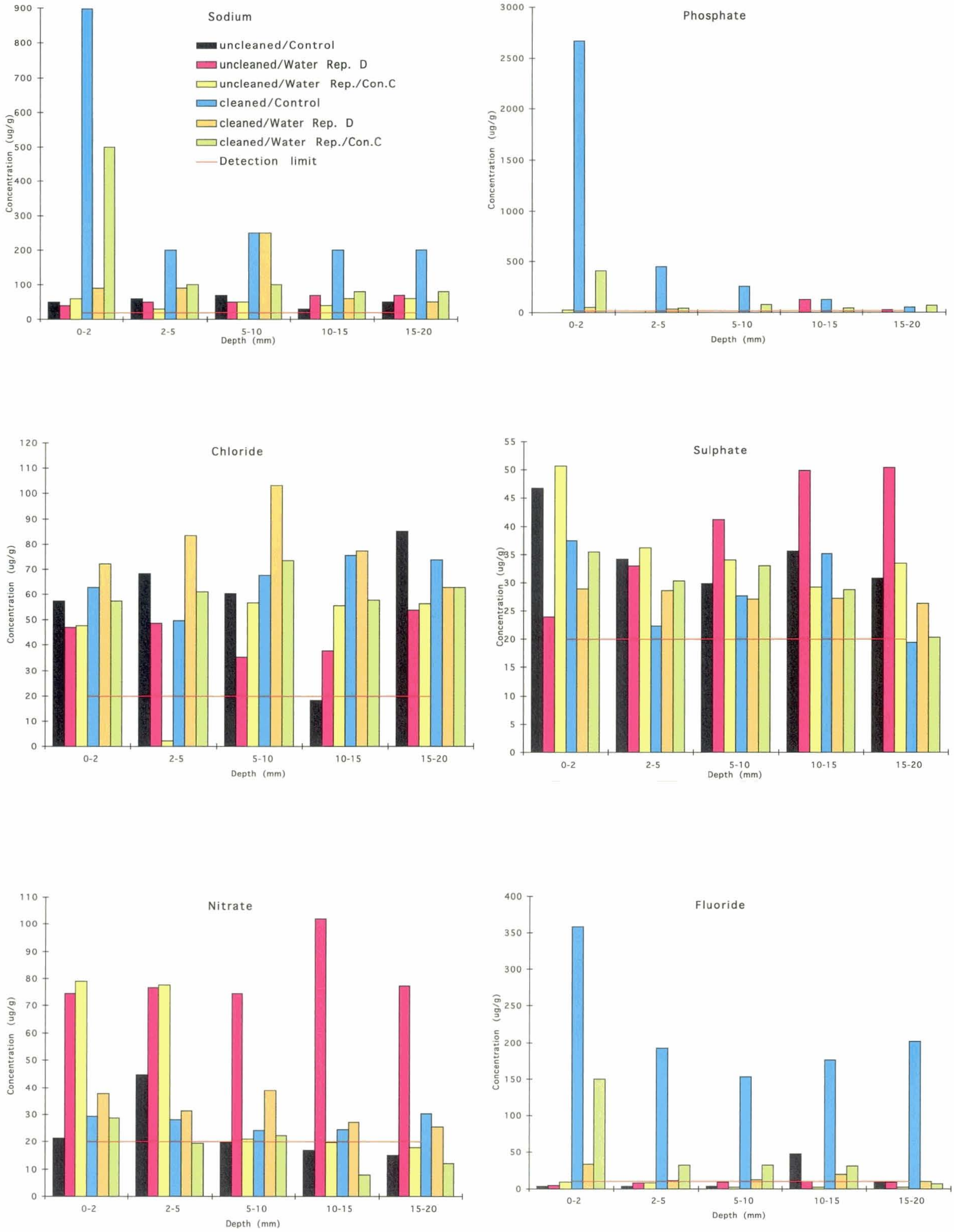


Figure 58c ***Fresh Clashach sandstone.*** *Soluble ions in treated or untreated blocks of sandstone before and after chemical cleaning.*

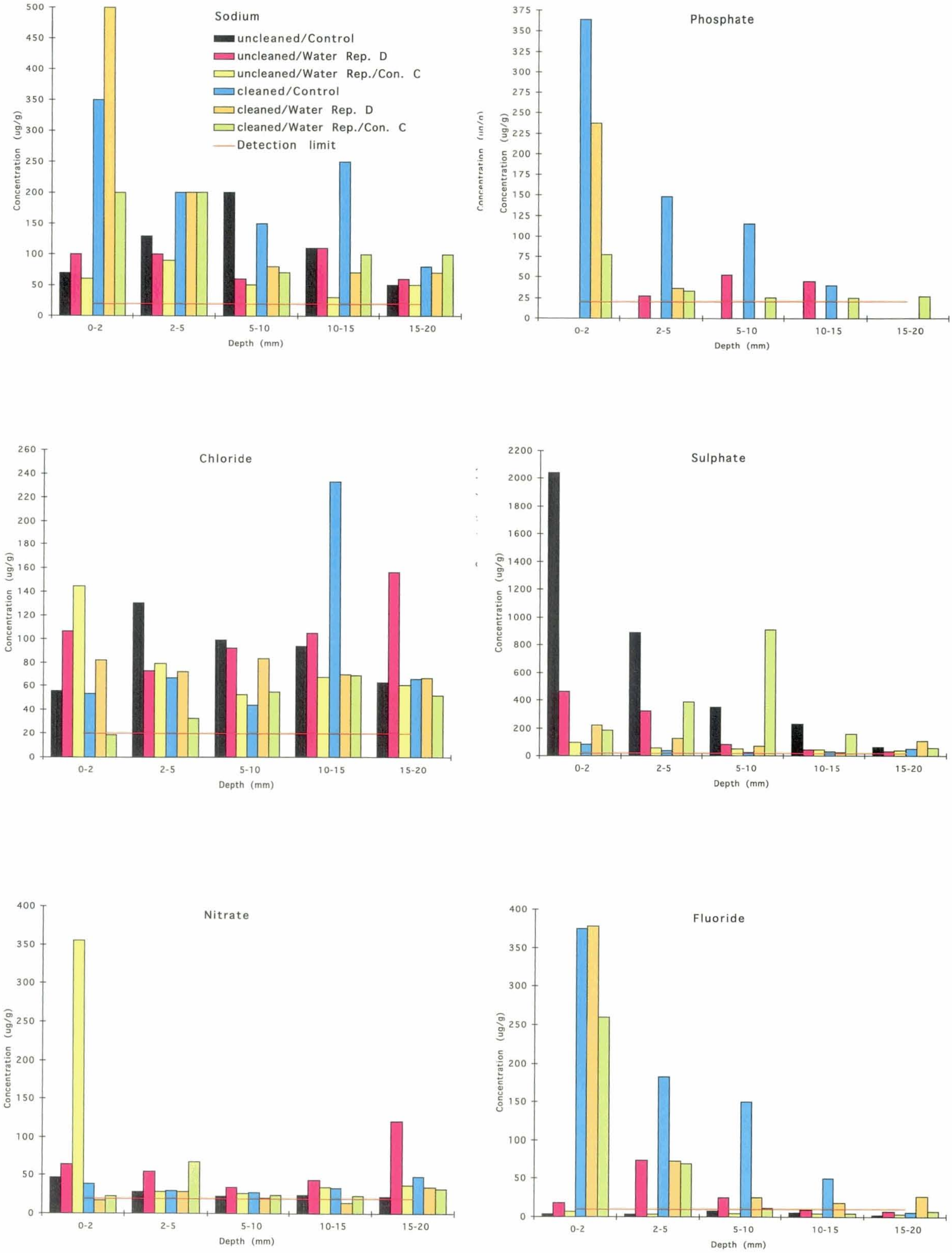


Figure 58d ***Soiled Clashach sandstone.*** *Soluble ions in treated or untreated blocks of sandstone before and after chemical cleaning.*

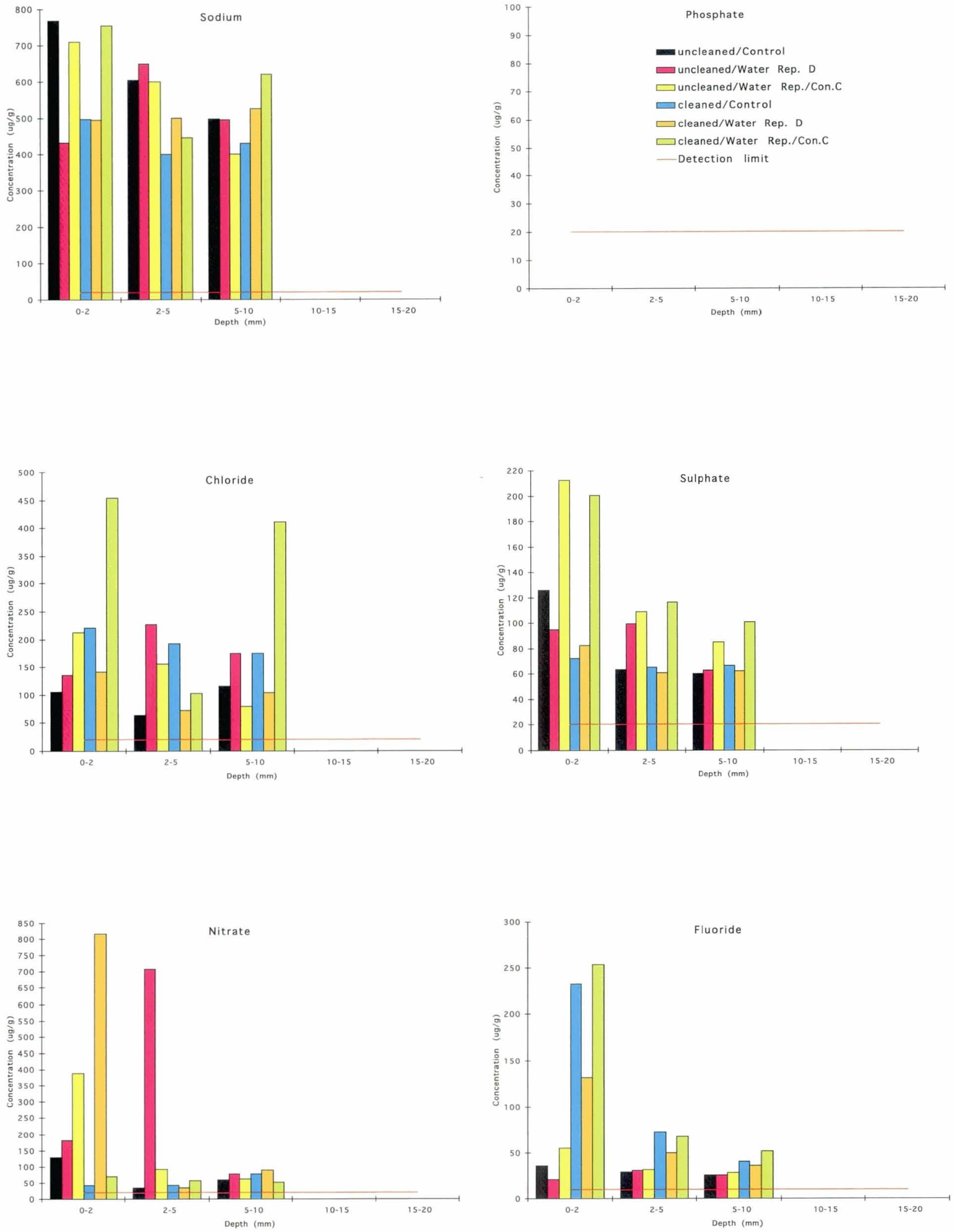


Figure 58e ***Fresh Leoch sandstone.*** *Soluble ions in treated or untreated blocks of sandstone before and after chemical cleaning.*

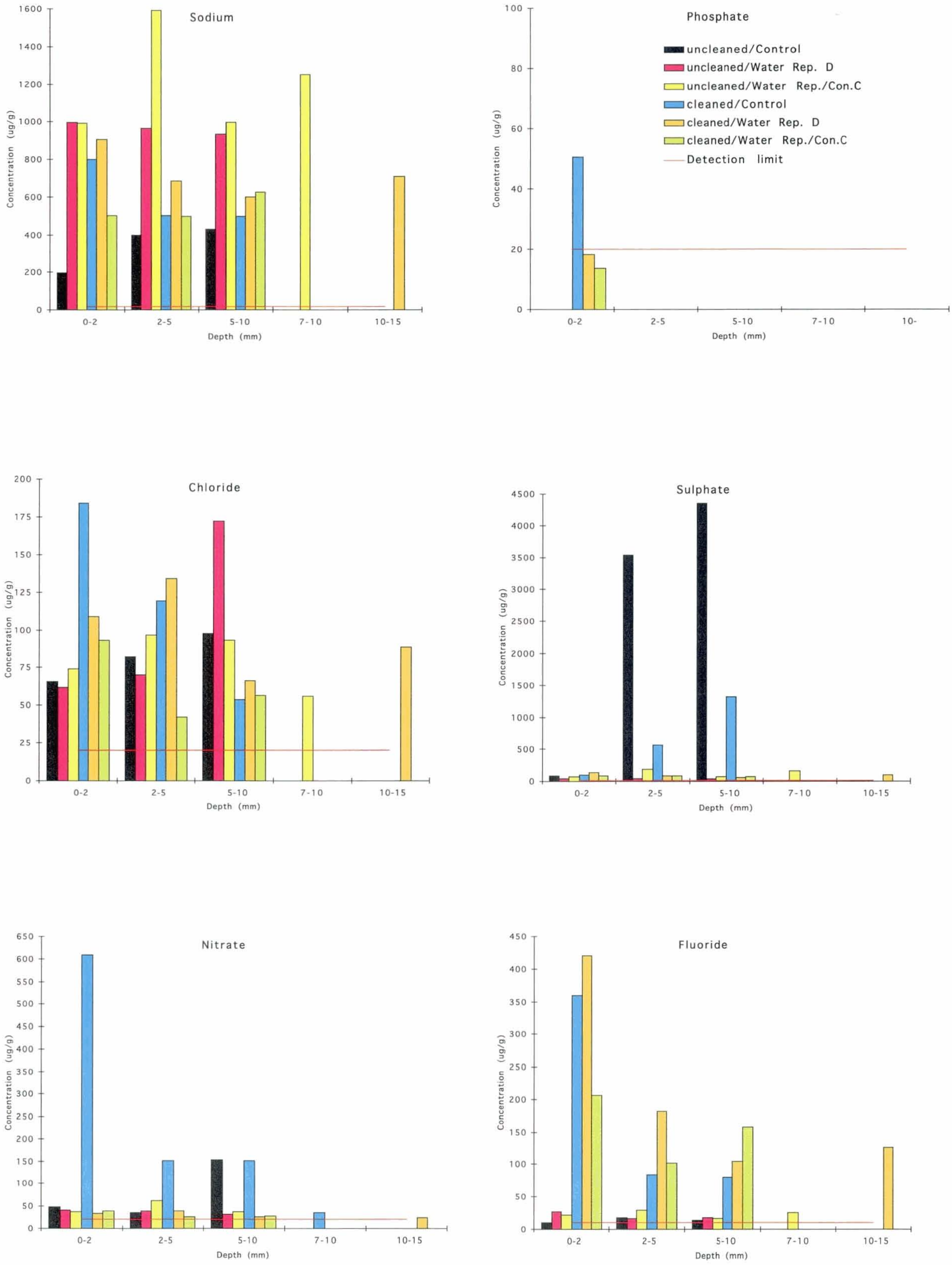


Figure 58f ***Soiled Leoch sandstone.*** *Soluble ions in treated or untreated blocks of sandstone before and after chemical cleaning.*

The mean concentrations of soluble sodium, fluoride and phosphate over the 20 mm depth of sampling (10-15 mm on Leoch sandstone) are shown in Figure 59. These are the ions which could be introduced into the sandstones as a result of chemical cleaning.

For fresh Leoch sandstone there was no evidence of any retention of sodium or phosphate after cleaning. Fluoride levels were higher after cleaning but there was no great difference between the amounts retained in treated (Water Repellent D or Water Rep./Con. C)and untreated samples. Soiled Leoch samples had low phosphate levels after cleaning. There was evidence of sodium and fluoride retention but no great difference was noted in the amount retained by treated and untreated sandstones.

For the more porous sandstone types (Locharbriggs and Clashach) there was clear evidence of differences in chemical retention of sodium, fluoride and phosphate in both fresh and soiled samples. Sodium, fluoride and phosphate residues were all higher in the fresh, untreated sandstone than in the soiled, untreated sandstones. This may be caused either by the greater permeability (Section 4.4.5) of the fresh sandstone or by chemicals being "used up" in the removal of soiling from the samples.

Sodium residues in treated (Water Repellent D and Water Rep./Con. C) sandstones were all fairly similar whether they were soiled or fresh. The difference between sodium retention in treated and untreated samples was greatest for fresh sandstones, the fresh, treated sandstone having about 20-50% of the level of sodium found in fresh, untreated the sandstone indicating that the treatments significantly reduced sodium retention in these stone types. The difference in sodium residues between treated and untreated, soiled sandstones was less although the treated samples did have less residual sodium, about 65-90% of the levels in the untreated samples.

Fluoride retention in fresh, treated (Water Repellent D and Water Rep./Con. C) sandstones was about 10-25% of its levels in fresh, untreated sandstones indicating that the water repellent (Water Repellent D) and the consolidant (Water Rep./Con. C) treatments had both substantially reduced retention of soluble fluoride in these samples. The differences were lower for soiled sandstones, levels in the treated samples being about 50-80% of those in the untreated samples.

Residual soluble phosphate levels in the treated (Water Repellent D and Water Rep./Con. C), fresh sandstone samples were only about 5-20% of their levels in untreated, fresh sandstone indicating that the treatments significantly reduced phosphate retention in these stone types. The differences were lower for soiled sandstones, levels in the treated samples being about 25-50% of those in the untreated samples.

These results indicate that both the water repellent (Water Repellent D) and the consolidant (Water Rep./Con. C) treatments were capable of substantially reducing the levels of retention of stonecleaning chemicals immediately following stonecleaning. There appeared to be little difference between these two treatments in terms of the effect they had in reducing chemical retention. For fresh sandstone, both Water Repellent D and Water Rep./Con. C treatment reduced the levels of chemical retention to approximately 20% of that in untreated sandstone. For soiled sandstone, water repellent/consolidant treatment reduced the levels of chemical retention to approximately 60% of that in untreated sandstone.

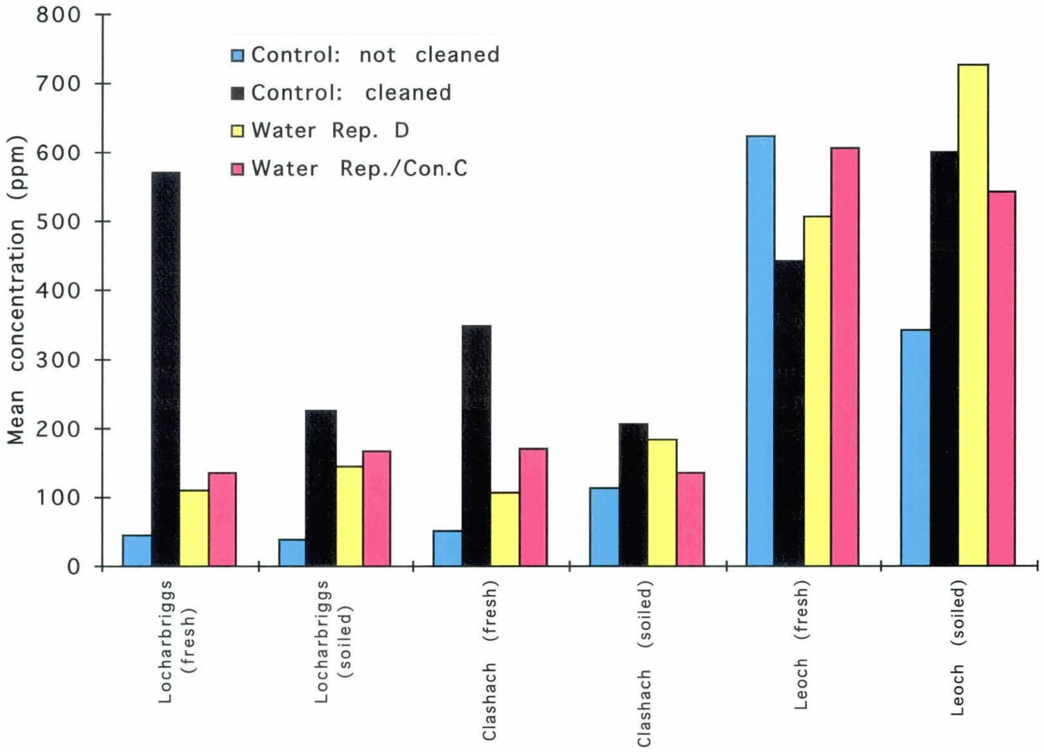


Figure 59a *Mean concentration of sodium in depth drilling samples from chemically cleaned sandstones.*

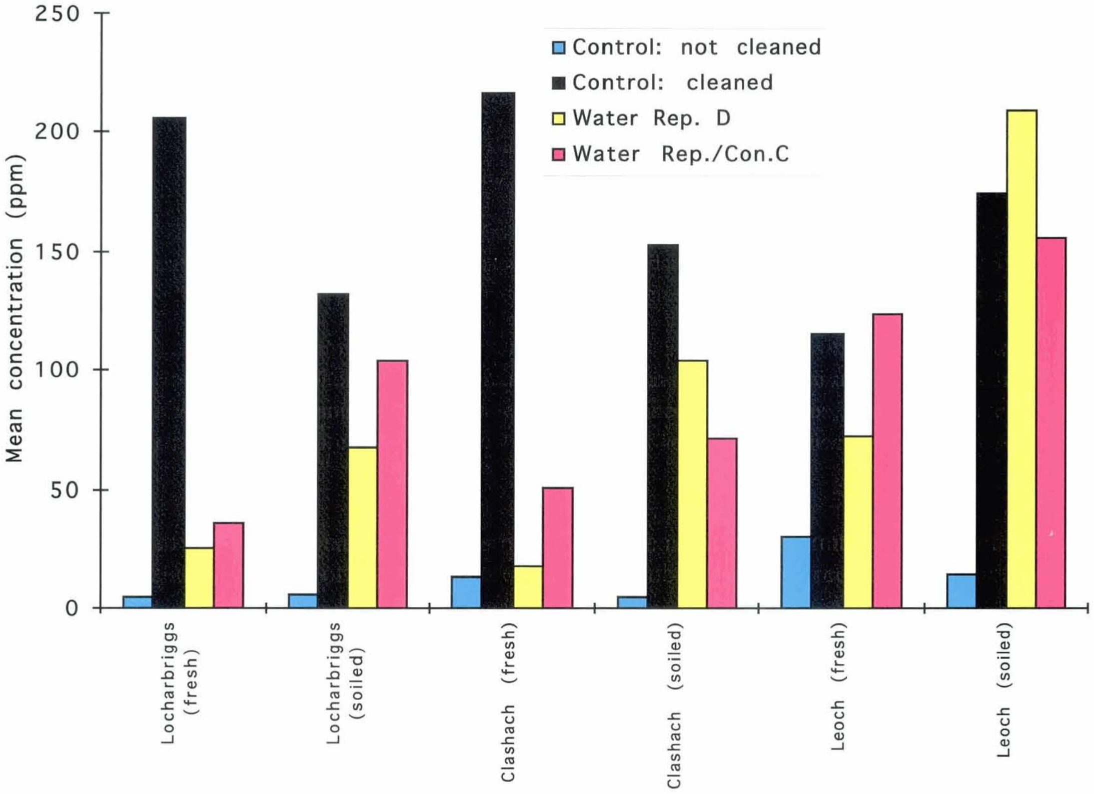


Figure 59b *Mean concentration of fluoride in depth drilling samples from chemically cleaned sandstones.*

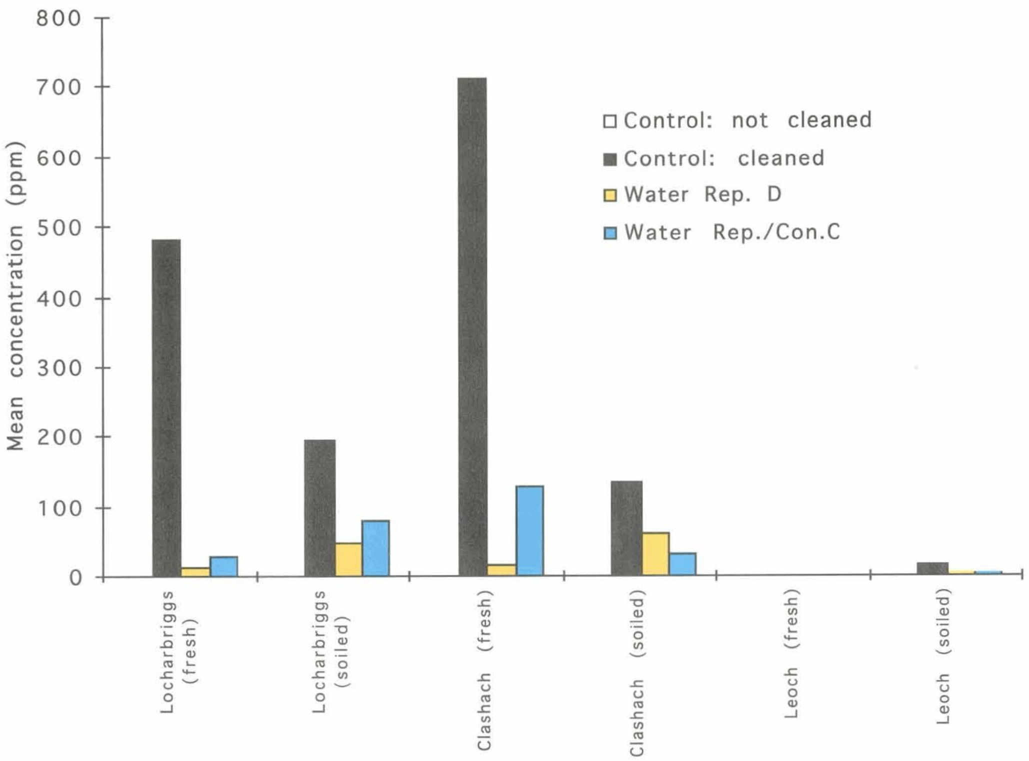


Figure 59c Mean concentration of phosphate in depth drilling samples from chemically cleaned sandstones.

4.7 Monitoring soiling rates with selected water repellents

It was found during earlier trials that, when applied to carbon disks, some water repellent treatments did not fully dry out over a period of several months. Since it is possible that this could encourage soiling of a treated substrate it was decided to apply these treatments to small samples of sandstone which would have their colour and lightness monitored to determine whether they soiled faster than untreated sandstones or sandstones treated with materials which do not remain tacky.

Selected samples (50x50x15 mm) of Clashach, Locharbriggs and Leoch sandstone were treated with Water Rep./Con. C and Water Repellent D on 11 July 1997 and with Water Rep. F and Water Rep. G on 15th July 1997. Of these treatments Water Rep./Con. C dried out completely when applied to a carbon disc, while Water Repellent D, Water Rep. F and Water Rep. G remained tacky for several months (at least). Two replicates were made of each sample. One set of sandstones remained untreated as controls. The samples were allowed to mature for a period of 3 weeks after which they were placed outside in a wooden frame at an angle of 45° to weather. Colour and lightness changes were monitored and the results are shown graphically in Figure 60. Dates of when colour measurement were taken were:

5 Jul 97	Before treatment
1 Aug 97	After treatment with water repellents
9 Oct 97	" " " " "
2 Dec 97	" " " " "
13 Jan 98	" " " " "
12 Feb 98	" " " " "
8 Jan 99	" " " " "

Colour and lightness changes on initial application of the treatments varied. However, the pattern of colour and lightness changes observed on the samples following application of the treatments was very similar in all cases.

Comparing the lightness and colour changes from after treatment (1st Aug 97) until the last colour measurement was obtained (8th Jan 99) it can be seen (Table 27) that there was no suggestion that samples treated with tacky water repellents (Water Repellent D, F or G) showed any exceptional colour or lightness changes compared to the control samples or those treated with Water Rep./Con. C.

It would appear therefore that although some of the water repellents remained tacky when applied to carbon discs, that this did not (over an 18 month period) increase the rate of soiling of sandstones to which the water repellents had been applied.

Clashach sandstone	L*	a*	b*
Control	-8.6	-3.1	3.4
Water Rep./Con. C	*-7.4*	*-2.8*	*0.6*
Water Repellent D	-3.6	-4.3	0.1
Water Rep. F	-8.8	-4.4	0.6
Water Rep. G	-10.6	-5.1	4.6
Leoch sandstone			
Control	-6.9	-0.7	3.2
Water Rep./Con. C	-5.4	-0.5	3.5
Water Repellent D	-4.1	-0.5	2.2
Water Rep. F	-4.3	-1.1	3.1
Water Rep. G	-6.1	-1.2	4.4
Locharbriggs sandstone			
Control	-7.6	-4.9	1.1
Water Rep./Con. C	-4.8	-5.3	0.0
Water Repellent D	-4.0	-6.8	1.6
Water Rep. F	-3.7	-4.7	0.5
Water Rep. G	2.6	-5.4	1.5

Table 27 Colour and lightness changes on samples from after their treatment until the last colour data were obtained.

4.8 Re-application of treatments to previously treated panels

It is possible that in some circumstances more than one consolidant treatment might be required on a sandstone, or may be applied inadvertently. While a deeply penetrating consolidant treatment might be useful for stabilising a sandstone which was prone to decay over several centimetres depth, these treatments may fail to stabilise the immediate surface, since solvent washes following treatment appear to reduce the strength of the outer few centimetres (Section 4.4.3). In such a case, application of a consolidant designed specifically to stabilise the outer few millimetres may be necessary.

To test the outcome of this type of treatment, small areas of previously treated test panels (Consolidant A and Water Rep./Con. C) were marked off for re-treatment with Consolidant B. Prior to re-treatment the colour and water absorption of these areas was assessed. Consolidant B has been applied to these areas using the same methodology as was established previously.

Table 28 shows the results in terms of colour changes. These results show that treatment with Consolidant B on top of pre-existing treatments (in this case Consolidant A and Water Rep./Con. C) can result in more intense darkening of the stone surface - about 5-6% more darkening than was caused by any single treatment. Visually, the effect of Consolidant B on the previously treated Water Rep./Con. C panel was more pronounced than re-treatment of the Consolidant A panel.

The longer term effects of applying two consolidant treatments of this type are unknown as, at the time of writing, the re-treated test areas had only been weathering for a few months.

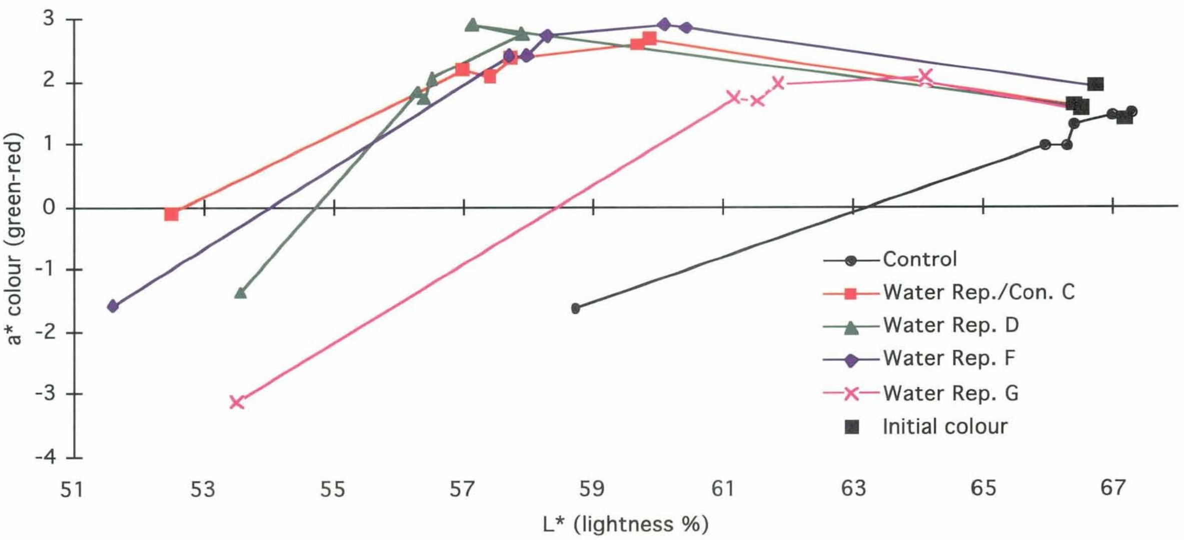


Figure 60a Colour changes on ***Clashach sandstone*** *samples used for monitoring soiling rates on samples treated with tacky water repellents.*

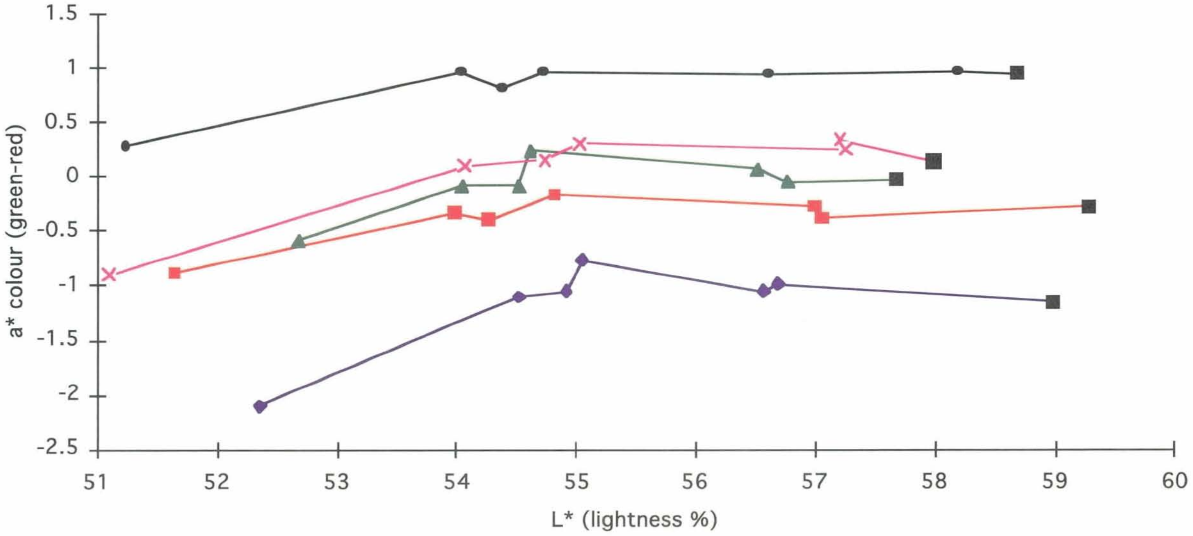


Figure 60b Colour changes on ***Leoch sandstone*** *samples used for monitoring soiling rates on samples treated with tacky water repellents.*

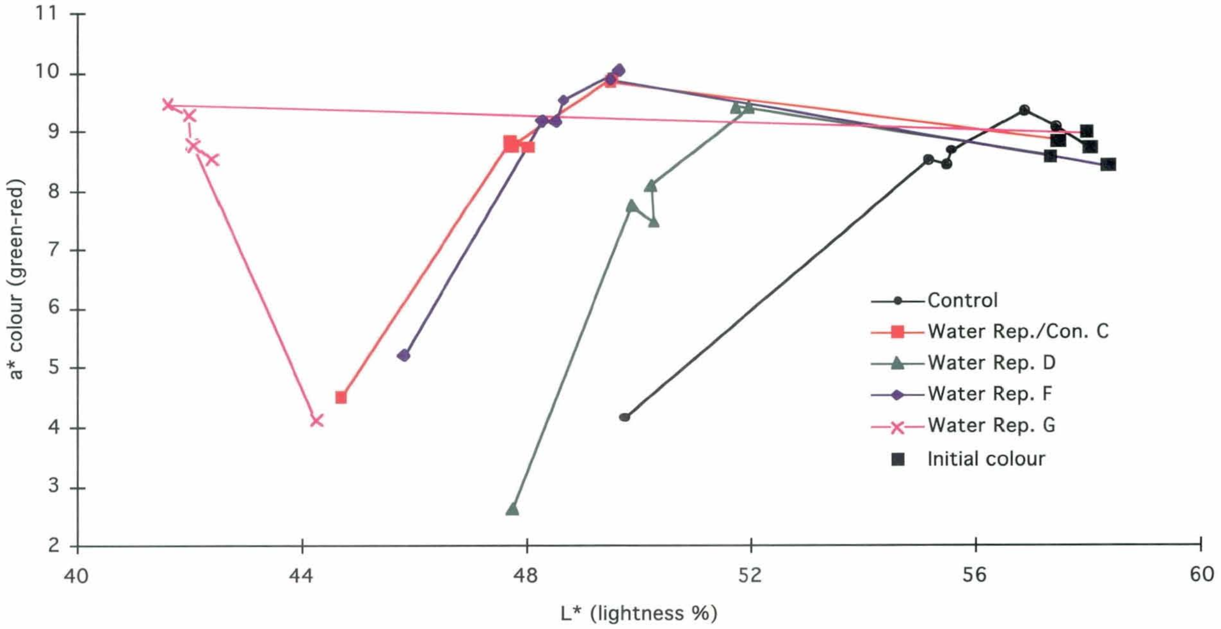


Figure 60c *Colour changes on* ***Locharbriggs sandstone*** *samples used for monitoring soiling rates on samples treated with tacky water repellents.*

Treatment	L*	a*	b*
Untreated	53.0	4.4	13.4
Consolidant A	51.6	3.7	13.6
Water Rep./Con. C	53.6	4.1	14.3
Consolidant B	51.4	4.3	14.1
Consolidant A + Consolidant B	46.5	3.7	14.0
Water Rep./Con. C + Consolidant B	47.1	4.5	14.0

Table 28 *Mean colour of fresh sandstones (Locharbriggs, Clashach, Stainton and Leoch) on test panels after various treatments.*

5 FIELD DATA

5.1 Pre-existing information on field treatments

The information given below has been summarised from information obtained from Historic Scotland. Further cores were taken from the sites for analysis. Since the stone was relatively fragile and it was essential to obtain cores with the least damage to the surrounding stone, hydraulic coring was essential to obtain intact cores. Dr Martin Kirk from Kirk Natural Stone Ltd was contracted to undertake the coring, and contributed advice and expertise in its developmental use in this context on test samples at Arbroath Abbey. Hydraulic coring has advantages over more commonly used coring systems:

- opportunity to run at very low speeds to allow controlled or hand positioning on weathered surfaces
- no kicking off the surface which would be found with high speed cores
- ability to stop and start the core bit with no jolting action
- ability to slow and stop mid coring to allow water washing of surface
- ability to remove the core bit slowly from the wall with no jolting action

Some of the cores failed to hold together or showed areas of structural loss. However where this was caused by general fracturing in the core barrel or by splits along existing mineralogical boundaries this was not considered relevant to the consolidation. On the Arbroath (2) and Dunkeld (3) samples, surface delamination was observed. However, it was unclear whether the consolidants caused the delamination, or held together what would otherwise have delaminated. Analysis of the sides of core holes can give clues to the existence of contour scaling.

5.1.1 Elgin Cathedral: Recess with effigy of Bishop John Pilmore

Notes on treatment (taken by Historic Scotland)

Treatment took place in the spring of 1986. A covered scaffold was erected over this tomb in order that it could be dried out to allow "Nonformale" resin consolidation to take place on one half of the canopy hood. The effigy required only a light clean to remove bird droppings and grime.

The Nonformale Method:

Sheltered, dried and free of loose dirt (especially if possible from behind the flakes), the stone is impregnated alternately several times with a resin mixture and with solvent. The resin mixture contains the following:

- 1 part by volume of 30% Paraloid B-72 in a non-polar solvent blend (typically, 45% each of toluene and xylene, with 10% of white spirit or amyl acetate, or similar solvent),
- 1 part by volume of silicone Dri Film 104 supplied in a 70% solution by General Electric, and
- 8 parts by volume of 1,1,1-trichloroethane

This fluid is liberally brush-fed through a strong absorbent tissue film both to strengthen the flakes and to make them marginally more flexible. The resin alternates at two or three day intervals with similar feeds of pure trichloroethane in order to take resin by degrees through the flakes and into the body of the stone, so avoiding potentially harmful superficial concentration. This step is accompanied by gentle pushing upon the saturated flakes to physically reunite as much of each as possible with the underlying stone. The sequence of resin followed by solvent is repeated up to six times, or more if necessary.

Consisting of small overlapping paper squares, the tissue film is held in place with a water-soluble adhesive (diluted wallpaper paste with a drop of disinfectant will do). Its purposes are to separate stone from brush, to act as reservoir for the resin mixture, and to secure saturated flakes as they are eased back into place over several working sessions. The tissue support remains in position until the resin has thoroughly hardened after the final application of pure solvent – up to a month or more, depending upon local conditions. It is removed by swabbing with acetone or purified water according to how much resin is left in it.

Observations made on 10th October 1996

The sandstone was fine-medium grained, buff in colour and probably calcareous. On both the treated and untreated areas there was moderate surface soiling. In some areas there was extensive development of hardened surface crusts with detachment at about 1-2 mm depth. In sheltered areas on both the treated and untreated sandstone there was evidence of granular disintegration of the surface as sand grains were found in crevices and grains were easily dislodged on brushing by hand.

The treated area on the right side was much more decayed than the untreated area to the left (about 75% surface loss compared with about 10% respectively). However, it is unclear how much decay was present before treatment as the only photo we have shows the right side covered with tissue prior to (?)consolidation. As well as can be judged from the photo, decay was more advanced on this side before consolidation but some areas of stone have been lost since 1986.

Much of the surface of the "treated" sandstone showed no obvious evidence of consolidation. The colour of much of the stone (about 75% of the surface area) appeared natural and unsoiled. About 25% of the surface appeared darker and moderately soiled. It is possible that this darker surface is all that remains of the original treated surface with the rest having been lost or the treatment deteriorated over the intervening decade. If the darker surface was what remained of the treated surface then the treatment appeared to have penetrated no deeper than the outer 1-2 mm of the sandstone.

Small (about 1-2 mm diameter) spots of white efflorescence (sampled) were noted on parts of the consolidated sandstone. No similar efflorescences were noted on the untreated sandstone.

There were some old patches of mortar repair at the centre of the arch and below the arch. In the area under the arch there was extensive decay (few centimetres deep) of the underlying sandstone.

Consolidation treatment of this sandstone does not appear to have been successful over 10 years.

5.1.2 Huntly Castle: Small fireplace

Notes on treatment (taken by Historic Scotland)

The time of treatment is not known.

Description:
Early 17th Century carved fireplace, two jambs (one [word indistinct]) lintel featuring two medallion portraits with arms and mottoes.

Material:
Delgaty free sandstone.

Condition:
R/H jamb The R/H jamb - v. friable with large delamination - previous been re-attached with epoxy resin.

Lintel (BRESS) Multitude of superfluous repairs upon lintel with some minor delaminations. R/H medallion portrait is darker in complexion due perhaps to previous shellac/meths consolidation process. Surface appears..... [sheet ends here]

Treatment, materials used, result:
The jamb which was extremely friable was faced up with bleach free tissue and a v. weak solution of starch paste. This area was then flooded with alternate applications of 8:1 trichloroethane, 30% Paraloid B-72 toluene, xylene, white spirit and pure trichloroethane. The consolidant was applied, then pure solvent was applied approx. half an hour later. Four applications of solvent per day for four days. The tissue was removed from the surface by flooding the tissue with propanone. The area was darker initially and took approx. 2 weeks to return to its natural appearance.

Observations made on 10th October 1996

The fireplace has been protected from rain and run-off by a perspex arch (since the time of treatment?). The condition of the sandstone was generally good. There were numerous small patches of repair (using epoxy resin?). There was little evidence of granular disintegration of the sandstone and almost no active spalling except for the right side of the fireplace where some small, thin flakes (<1 mm thick) were coming off with underlying granular disintegration. There were some hollow sounding areas on the sandstone over the fireplace which appear to have been stabilised by the consolidation treatment.

This consolidation treatment appears to have been successful up to the present time (1996).

5.1.3 Arbroath Abbey

Notes are available on the treatment of the bottom 0.5 m of columns at the west end arcade over the entrance carried out on 14th October 1976 (Table 29, Figure 61). The following information has been copied from a report (Note No. N(C) 18/78) by the Building Research Establishment dated March 1978 (Arnold *et al.*, 1978).

Type of stone:
Sandstone.

Type of decay:
Powdering.

Date of treatment:
14 October 1976.

Stonework treated:
The bases of two columns. The circumference of each column was 0.86 m, and the columns were treated to a height of 0.5 m.

Treatment:
One column was treated with Brethane containing 0.5% of a 12% solution of Manosec Lead 36 (equivalent to the standard formulation). The second column was treated with Brethane containing 1% of the same catalyst solution.

Nominal depth of treatment:
41-43 mm.

Observations at the time of treatment:
Application was by brush and tended to detach a certain amount of loose stone.

Subsequent observations:
The trials were inspected by W. Adams of the Stenhouse Conservation Centre, Edinburgh, on 25 January 1977. He reported "very good results - surfaces strengthened greatly and consistently overall. No optical change.

Porosity measurements:
Core samples were taken from each treated area and from adjacent untreated areas on 25 January 1977. Each core, approx. 80 mm in length, was divided into three pieces of approximately equal length. Water absorption properties are given in Table 4 *[These results have not been located].*

Additional notes on observations made are identical to those above with the addition of: "Sound and would seem by feel of core drill to about 2 inches deep. No sweating- due to sheltered nature of site. No optical change."

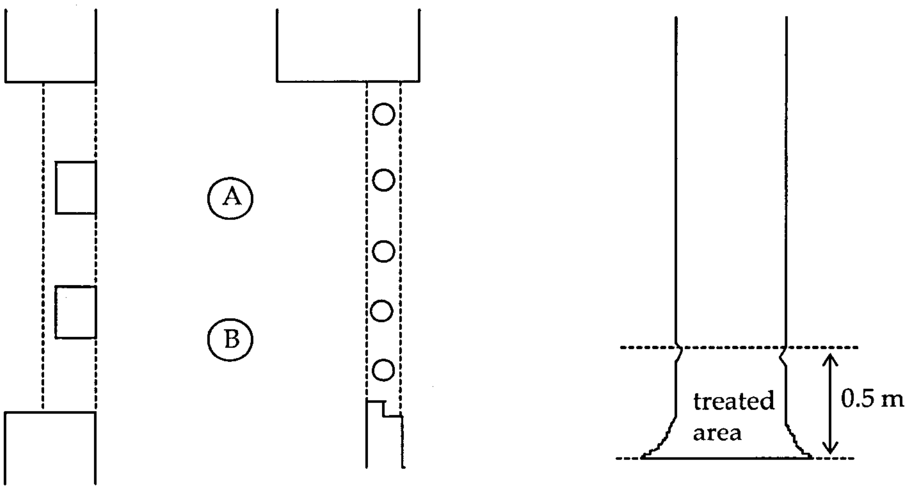


Figure 61 Location of treatments to columns at Arbroath Abbey.

Column	Treatment	Comments
A	For 500 mL batch: 330 mL methyltriethoxysilane + 175 mL meths/water (110 mL meths + 65 mL water) + 2.5 mL of 12% solution of Manasec(?) Pb 36 in white spirit	2 L of half dose catalyst resin was applied by brush.
B	For 500 mL batch: 330 mL methyltriethoxysilane + 175 mL meths/water (110 mL meths + 65 mL water) + 5 mL of 12% solution of Manasec(?) Pb 36 in white spirit	1.9 L of normal dose catalyst resin was applied by brush.

Table 29 Arbroath Abbey. Composition of treatments applied to of columns at the west end arcade over the entrance carried out on 14th October 1976.

The sandstone block cored in this project is shown in Figure 63. Coring was carried out using a hydraulic coring system on 18th February 1997. Two control cores were taken from untreated sandstone; one to RGU, one to BRE. Three core samples were taken from one sandstone in the Brethane treated site; one to RGU, two to BRE. It was noted that the treated core was significantly water repellent to a depth of 40 mm.

5.1.4 Dunkeld Cathedral

Treatment (Table 30, Figure 62) was carried out on 13th October 1976 on the east face of a column on the north arcade nave to the west side of a doorway (Figure 64). Height to the base of the treated area was 1.12 m from the top edge of the column base. The following notes (Arnold *et al.*, 1978) on the treatment have been located:

Type of stone:
Sandstone.

Type of decay:
Contour scaling.

Date of treatment:
13 October 1976.

Ambient temperature:
8°C.

Nominal depth of treatment:
35-55 mm.

Stonework treated:
Three blocks of stone in a column. The surface of each block measured approximately 0.45 x 0.25 [units indistinct].

Treatment:
One block was sprayed with Brethane containing 0.5% of a 12% solution of Manosec Lead 36; another was sprayed with Brethane containing 1% of the same catalyst solution; the third received a brush application of Brethane with 1% catalyst solution.

Observations at time of treatment:
Brush application tended to detach loose fragments of stone. Spray application overcame this problem and was generally easier to control.

Subsequent observations:
The trials were inspected by W. Adams of Stenhouse Conservation Centre, Edinburgh, on 24 January 1977. He reported "The three areas treated were overall greatly strengthened except locally on the two which were spray treated- Here small scales were hard but brittle. The three were sweating- indicating water repellence. There is a slight darkening which alters the optical quality [Other notes available add the following here: -very pronounced darkening of treated stones in tomb recess]. Brush treated stone best overall consolidation of surface due to removal of surface debris by brush action"

Porosity measurements:
Core samples were taken from each treated block and from an adjacent untreated block on 14 January 1977. Each core, approx. 80 mm long, was divided into three pieces of approximately equal length. Water absorption properties are given in Table 15 [This data has not been located].

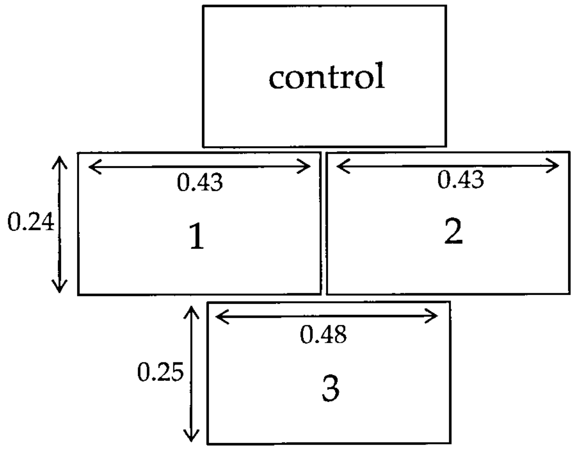


Figure 62 Locations of test panels on column at Dunkeld Cathedral.

[measurements given in metres]

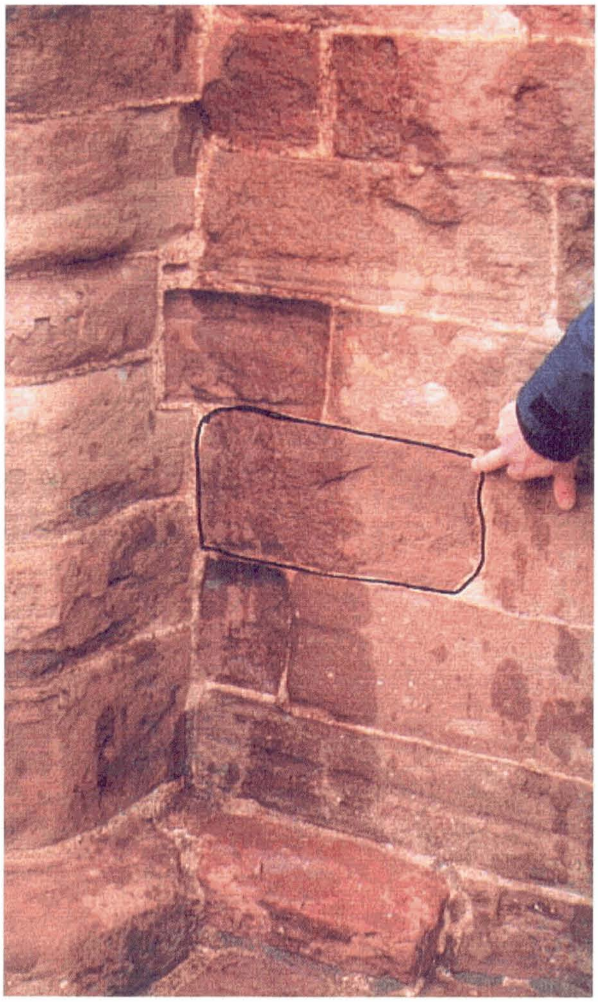


Figure 63 Sandstone block from Arbroath Abbey cored during this research project.

Figure 64 Treated area on column at Dunkeld Cathedral.

Panel	Treatment	Comments
1	For 500 mL batch: 330 mL methyltriethoxysilane + 175 mL meths/distilled water (110 mL meths + 65 mL distilled water) + 2.5 mL of 12% solution of Manasec(?) Pb 36 in white spirit	Spray application over 3 hours of 750 mL silane solution. Single dose.
2	For 500 mL batch: 330 mL methyltriethoxysilane + 175 mL meths/distilled water (110 mL meths + 65 mL distilled water) + 5 mL of 12% solution of Manasec(?) Pb 36 in white spirit	Spray application over 3 hours of 725 mL silane solution. Double dose.
3	No information available.	Brush application over 3 hours of 425 mL silane solution. Double dose.

Table 30 Dunkeld Cathedral. Notes on treatments carried out on 13th October 1976 on the east face of a column on the north arcade nave to the west side of a doorway.

Another treatment was carried out on a sandstone block above the tomb of Bishop Robert de Cardeny in the south wall (Figure 65). Application was of 400 mL of consolidant (no information on composition) over 2 hours.

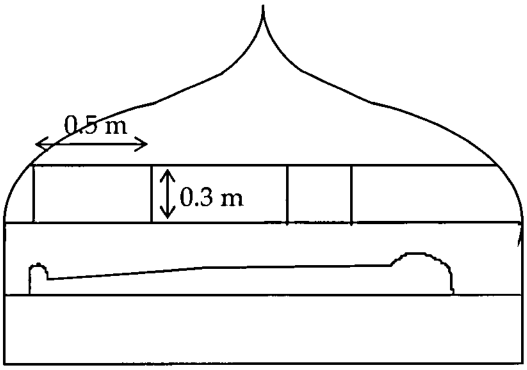


Figure 65 Treated area on tomb of Bishop Robert de Cardeny at Dunkeld Cathedral.

Coring of the columns previously cored in 1977 was carried out using a hydraulic coring system on 19th February 1997. One control core was taken from the same untreated sandstone that was used previously. Three core samples were taken, one from each of three consolidant treated sandstones; one to RGU (from panel 1), two to BRE (from panels 2 & 3).

5.1.5 Tantallon Castle

Treatment carried out on 3rd June 1974 on free standing section of wall beside cliff top (Figure 66 & 67). There was no prior treatment. All treatments were applied by brush.

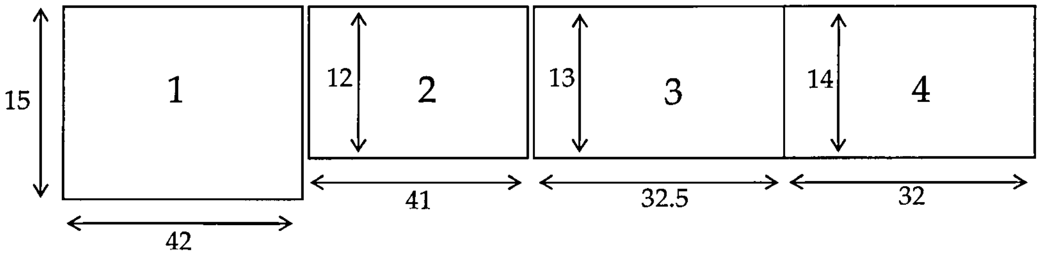


Figure 66 Locations of test panels on wall at Tantallon Castle. [measurements assumed to be given in centimetres]

Panel	Treatment	Comments
1	$SiMe(OEt)_3 + Si(OEt)_4$ (3 : 1 molar)	500 mL absorbed; panel brushed with water after treatment
2	$SiMe(OEt)_3$	500 mL absorbed; panel brushed with water after treatment
3	$SiMe(OEt)_3 + Si(OEt)_4 + H_2O$ containing 100 ppm HCl (3 : 1 : 6.5 molar)	<150 mL absorbed with difficulty
4	$SiMe(OEt)_3 + H_2O$ containing 100 ppm HCl (1 : 1.5 molar)	<150 mL absorbed with difficulty

$SiMe(OEt)_3$ = methyltrimethoxysilane

$Si(OEt)_4$ = tetraethoxysilane

Table 31 Tantallon Castle. Notes on treatment carried out on 3rd June 1974 on free standing section of wall beside cliff top

Additional coring of the previously cored blocks was carried out using a hydraulic coring system on 20th February 1997. One control core was taken from untreated sandstone. Four core samples were taken, one from each of four consolidant treated sandstones; two to RGU (from panels 1 & 2), two to BRE (from panels 3 & 4).

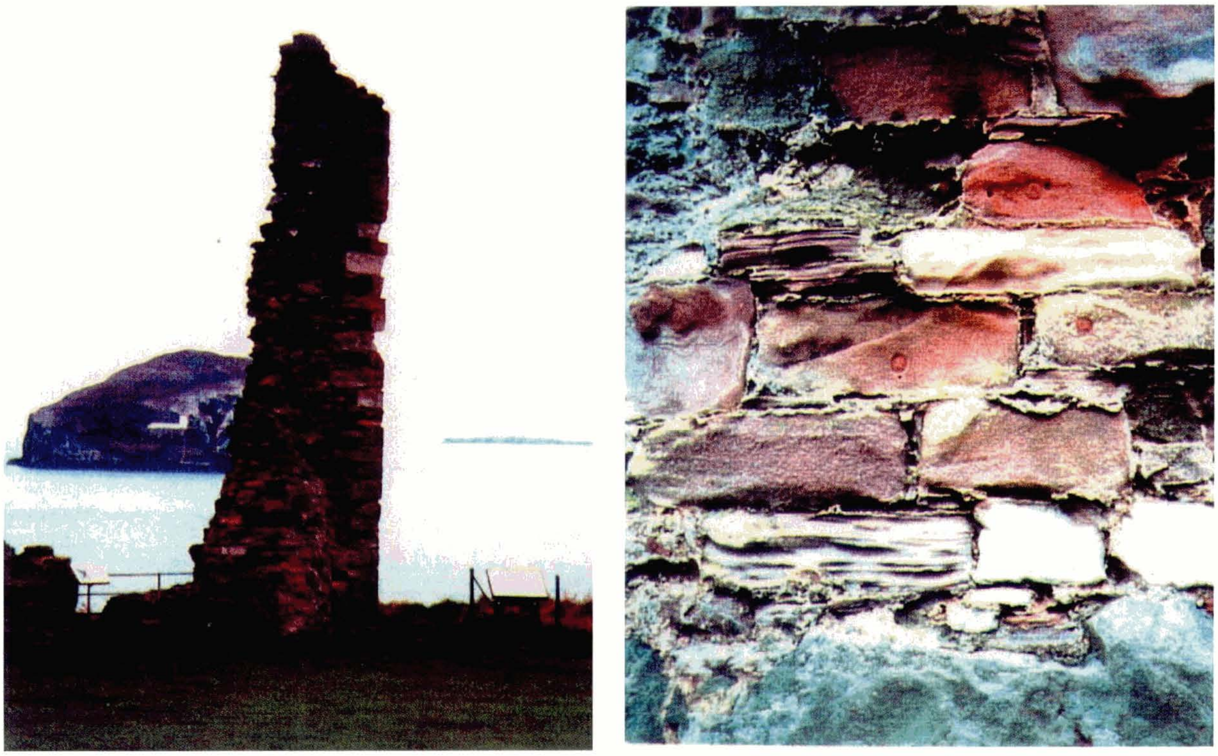


Figure 67 Location of test panel at Tantallon Castle.

5.2 Petrography results from field sites

The results of petrographic analysis of core samples from the field sites are shown in Figure 68 and Table 32. The control and treated samples from Dunkeld Abbey were very similar. The control and treated samples from Tantallon Castle varied slightly but were essentially very similar mineralogically. However, the control sample from Arbroath Abbey differed from the treated sample in that the control sample contained significant amounts of calcite (10%). The treated sample contained only trace amounts of calcite. Consolidant treatments were not visible in any samples under the microscope.

Arbroath control : calcareous litharenite (see Figure 68)

Arbroath treated 1: calcareous litharenite

Tantallon control : calcareous sub arkose

Tantallon treated 1: calcareous sub arkose

Tantallon treated 2: calcareous sub arkose

Dunkeld control : calcareous feldspathic litharenite

Dunkeld treated 1: calcareous feldspathic litharenite

	Detrital minerals (%)									Authigenic minerals (%)							
	qtz	orth	Ksp	plag	musc	bio	rock	heav	opq	qtz	flsp	calc	dol	kao	clays	chlor	fe-ox
Arbroath Control	20	5	<<1	<<1	<<1	<<1	44	<<1	1	0	0	10	0	5	10	<<1	5
Arbroath treated	25	10	<<1	<<1	1	<<1	51	0	<<1	<<1	<<1	<<1	0	0	10	<<1	3
Tantallon Control	77	5	1	1	<<1	0	1	<<1	0	1	0	5	0	2	5	0	2
Tantallon treated 1	85	5	<<1	<<1	1	1	0	<<1	<<1	0	0	4	0	0	2	0	2
Tantallon treated 2	75	10	<<1	<<1	<<1	<<1	0	<<1	<<1	<<1	0	8	0	0	2	0	5
Dunkeld Control	25	10	<<1	5	<<1	<<1	35	<<1	1	<<1	0	10	0	0	10	3	1
Dunkeld treated	24	10	<<1	2	<<1	<<1	40	<<1	0	0	0	10	0	0	10	2	2

(f): fresh
(s): soiled
qtz: quartz
orth: orthoclase feldspar
Ksp: potassium feldspar
plag: plagioclase feldspar

flsp: feldspar (type not defined)
musc: muscovite mica
bio: biotite mica
rock: rock fragments
heav: heavy minerals
opq: opaque minerals

calc: calcite
dol: dolomite
kao: kaolinite
clay: clays (not including kaolinite)
chlor: chlorite
fe-ox: iron oxides & hydroxides

Table 32 Results of petrographic analysis on field samples. Amounts of minerals are shown as percentages. "Detrital" minerals are the "sand grains" which make up the body of the sandstone. "Authigenic" minerals are minerals deposited during the formation of the sandstone, e.g. cements.

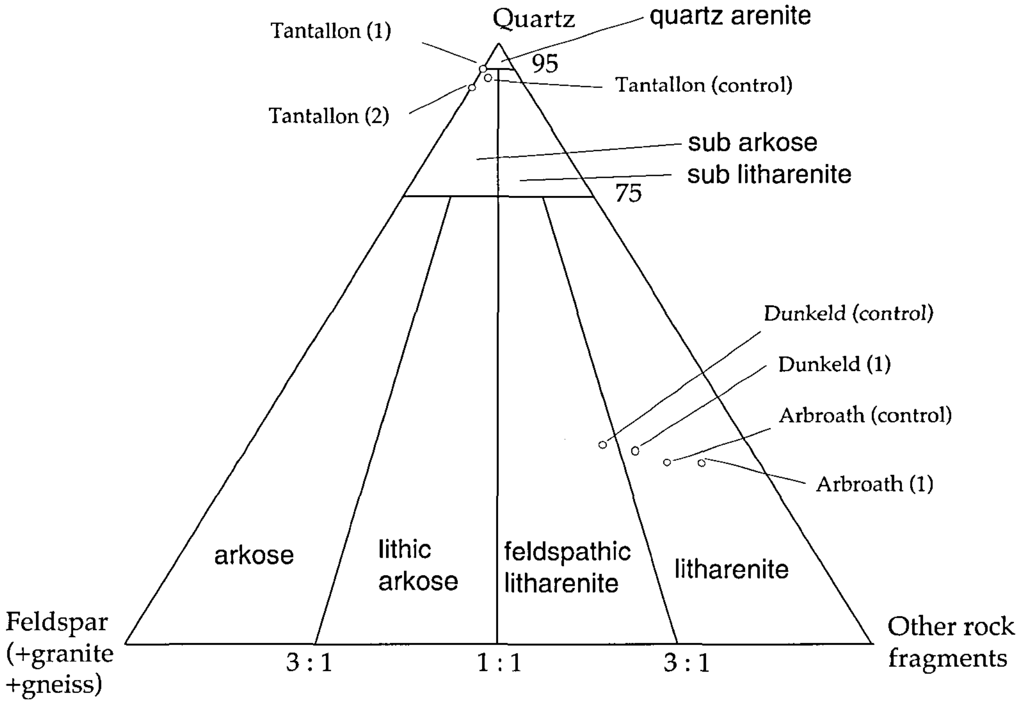


Figure 68 Ternary diagram used for determining the composition of sandstones from field sites.
(From: Adams, A.E., MacKenzie, W.S. and Guilford, C., 1984, *Atlas of Sedimentary Rocks Under the Microscope*. Longman)

5.3 Mercury porosimetry results for samples from field sites

Results of mercury porosimetry on samples from field sites are shown in Figure 69. Total effective porosity data are shown in Table 33.

	Controls		Treated	
Site	**Exterior**	**Interior**	**Exterior**	**Interior**
Arbroath Abbey	15.8	12.8	19.2	20.4
Dunkeld Cathedral	14.8	12.5	12.1	11.9
Tantallon Castle 1	22.9	24.4	24.7	24.7
Tantallon Castle 2	na	na	24.0	19.3

na: not applicable

Table 33 Results of mercury porosimetry of sandstone samples from field sites. Showing total effective porosity (%) for samples from the exterior and interior (beyond the maximum depth of penetration of treatments) of sandstones.

Results from Arbroath Abbey showed only a small difference (1.2%) in total porosity between the exterior and interior of the treated sandstone. However, there was a noticeable difference in the pore size distribution (Figure 69a). The untreated, interior of the sandstone showed peaks in porosity at about 230μm and 16μm. For the exterior of this samples, the same peaks in porosity were still seen, but they were reduced in height. This indicated that there may have been a loss in porosity due to the treatment applied to this sandstone. The treatment was still noticeable in the exterior 40 mm of the sandstone as water repellency.

Dunkeld Cathedral samples from the exterior and interior of a treated block showed little difference in porosity (Figure 69b). The external porosity was slightly higher and there was a slight increase in external porosity in the range 2-100 μm possibly as a result of weathering. There was no indication of blockage of porosity due to the consolidant treatment.

Results from Tantallon Castle (Figure 69c & d) showed no difference in porosity (24.7%) between the external and internal samples from the sandstone sample Tantallon 1. There was also no observable difference between the samples in pore size distribution. For sample Tantallon 2, the porosity of the untreated interior of the sample was lower (19.3%) than the treated exterior (24.0%). There was no shift in the position of the mode of PSD. The more porous exterior is likely to be a weathering effect.

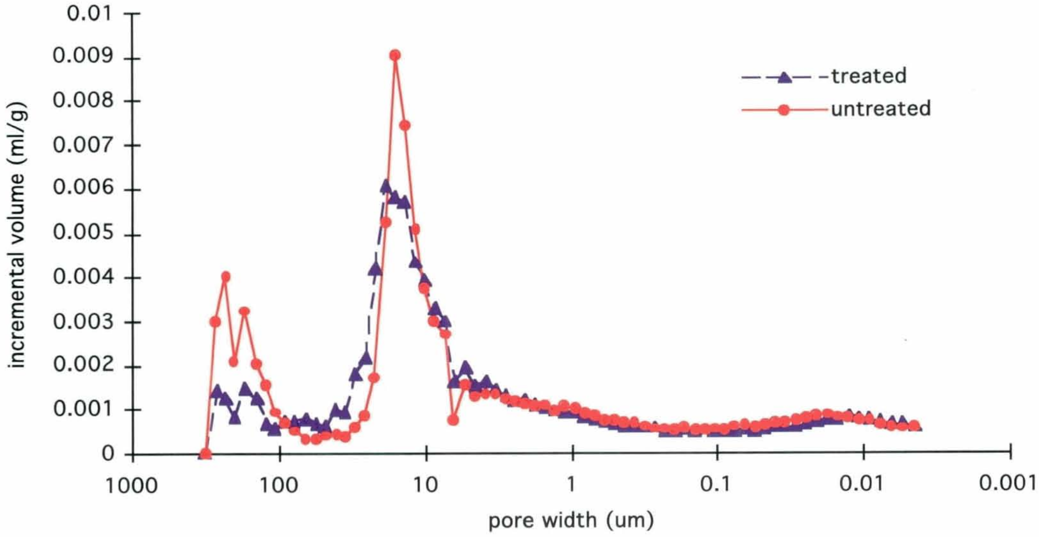


Figure 69a Mercury porosimetry results of pore size distribution measurements for treated (stone exterior) and untreated (stone interior) sandstone from ***Arbroath Abbey*** *(sample 4).*

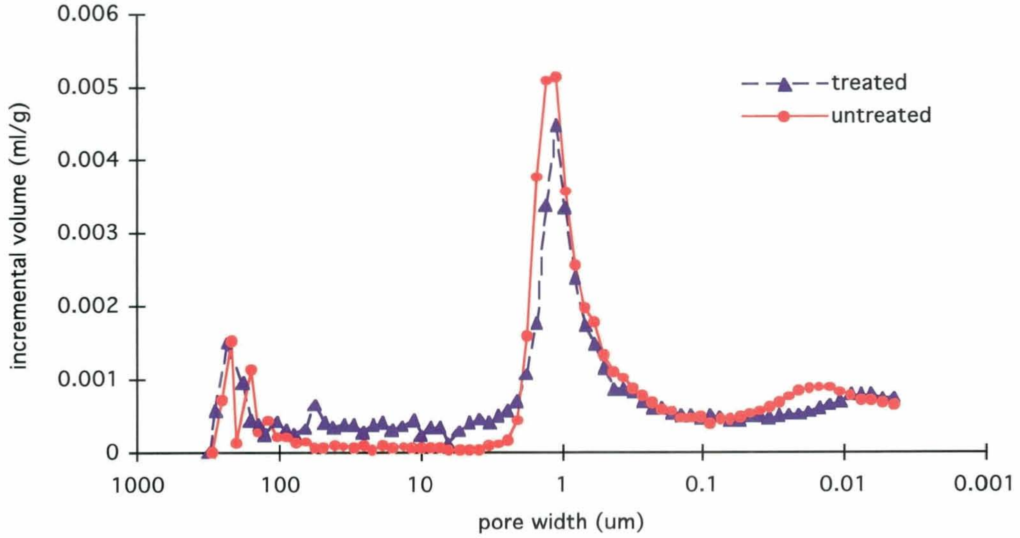


Figure 69b Mercury porosimetry results of pore size distribution measurements for treated (stone exterior) and untreated (stone interior) sandstone from ***Dunkeld Cathedral*** *(from panel 1).*

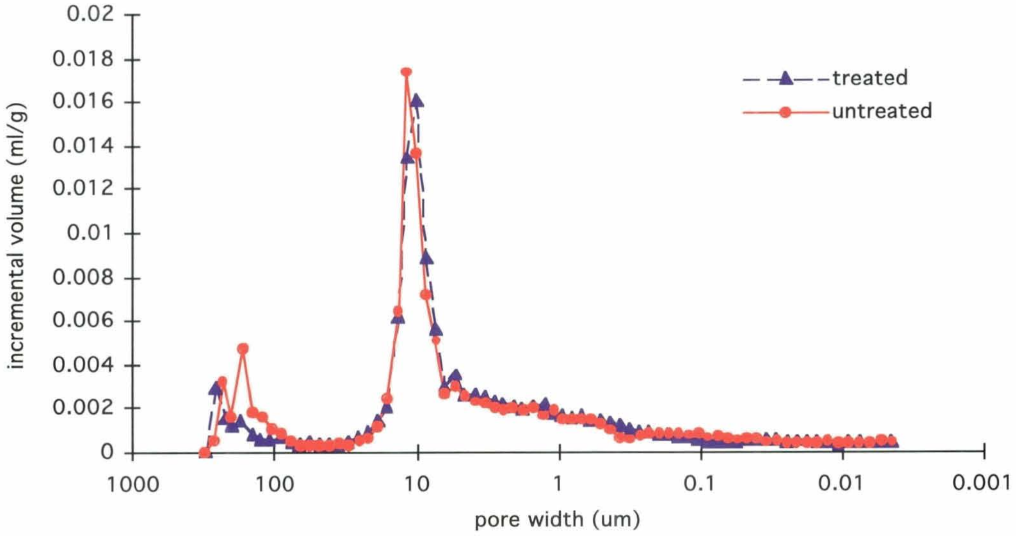


Figure 69c Mercury porosimetry results of pore size distribution measurements for treated (stone exterior) and untreated (stone interior) sandstone from ***Tantallon Castle*** *(from panel 1).*

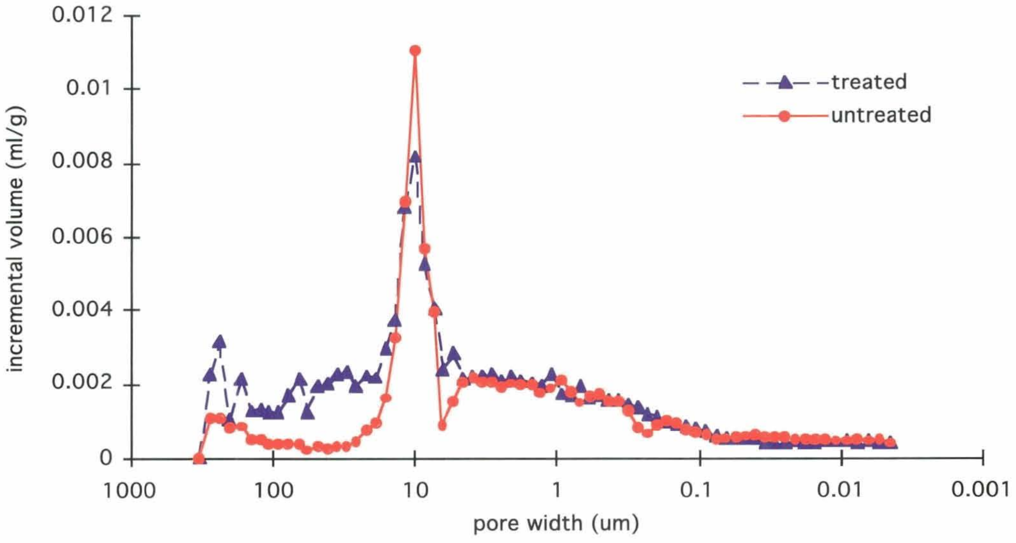


Figure 69d Mercury porosimetry results of pore size distribution measurements for treated (stone exterior) and untreated (stone interior) sandstone from ***Tantallon Castle*** *(from panel 2).*

5.4 Long term effects of consolidation

Visual and photographic examination of the dry cores and dry treated blocks did not show evidence of actual consolidation; however, application of water to the consolidated wall at Arbroath clearly showed the location of the treated areas as they 'wetted' differently, treated areas retaining obvious water repellency.

Unfortunately, it was not possible to show whether the treatments had decreased the rate of stone loss. This could only have been achieved if the blocks had been partially treated in clearly recorded locations. At all three sites, Dunkeld, Tantallon and Arbroath entire blocks were treated. As the blocks appear to weather at slightly different rates it is difficult to compare decay rates to the control block. However, it can be observed that the treatments do not appear to have dramatically increased decay or caused colour changes.

5.5 Depth of penetration

Treated cores from Arbroath, Dunkeld and Tantallon all showed hydrophobic properties which were due to the consolidation about 20 years earlier. As a result the depth of penetration could be determined (Table 34) as described in Section 3.3.5. A combination of water drop tests and observation of water evaporation was carried out on the cores.

Site & core no.	Panel no.	Treated / untreated	Length of core (mm)	Depth penetration (mm)
Arbroath control		untreated	150	0
Arbroath 1		treated	103	45
Arbroath 2		treated	145	35
Arbroath 3		treated	64	25
Dunkeld control		untreated	100	0
Dunkeld 2	2	treated	140	18
Dunkeld 3	3	treated	100	28
Dunkeld 1	1	treated	47	26
Tantallon control		untreated	135	0
Tantallon 2	2	treated	60	15 (unclear)
Tantallon 3	3	treated	90	35
Tantallon 4	4	treated	118	65

Table 34 Depth of penetration of water repellency of consolidant in field sites. Panel numbers as shown in Tables 30 & 31.

As there were measurable hydrophobic properties in the treated sandstones, this was clear evidence of the continued presence of the consolidants or related components. The depth of penetration of the consolidants varied from 18 to 65 mm into the stone. In all treated cores the consolidated region was also still stable. There was no sub-consolidated surface failure. In some of the cores the depth of the consolidants was substantial enough to probably avoid surface delamination as salts would be unlikely to crystallise several centimetres below the surface.

6 ESTABLISHMENT OF TEST PANEL FOR LONG TERM MONITORING AT HOLYROOD PARK

A field site for the long term monitoring of the effects of consolidants and water repellents on sandstone has been set up on a wall in Holyrood Park. The location of the test site is shown in Figure 69. The test panel area is shown in Figure 71.

Six sandstone blocks were chosen for application of three different consolidants / water repellents. Each treatment was applied to two sandstones and surrounding mortar. The materials used were Consolidant B (a consolidant), Water Rep./Con. C (a consolidant/water repellent) and Water Repellent D (a water repellent). Treatment was carried out on 18th September 1997. A series of tests were carried out on the test panel prior to treatment. The test panel area was photographed and the surface area of each block was measured. Colour measurements were taken of the surfaces of both the sandstones and mortar. Water absorption measurements were carried out on the sandstone blocks. One block was drilled for depth profiling for soluble salt residues. All sandstone blocks were cored prior to application of the consolidant or water repellent. Cores were also taken from the mortar. The amount of consolidant / water repellent applied to the sandstones was measured by volume.

It is hoped that regular monitoring of the test panel could continue for a number of years. This could involve additional coring, however, much useful data could be gathered from non-destructive monitoring which should include: photography of individual blocks, measurement of colour, measurement of water absorption, visual assessment of biological growths and visual assessment of presence of any decay or efflorescences.

Sampling by coring and analysis of stone colour (Figure 72) and water absorption (Figure 73) was made before application of the consolidants and water repellents. Depth profiling of drill samples from Stone 4 was carried out to examine soluble salt residues (Figure 74).

Stone number	Stone colour	Treatment	Amount applied (mL/m^2)
1	**blonde**	**Water Repellent/Consolidant C**	**1927**
2	**blonde**	**Water Repellent D**	**1734**
3	**blonde**	**Consolidant B**	**1280**
4	**red**	**Water Repellent/Consolidant C**	**2999**
5	**red**	**Water Repellent D**	**1200**
6	**red**	**Consolidant B**	**1192**

Table 35 Holyrood test panel. Sandstone number, treatment and surface area.

6.1 Colour analysis

Results from colour analysis of the test panel sandstones and mortars are shown in Figure 72.

6.2 Water absorption

Results from measurement of water absorption are shown in Figure 73.

6.3 Depth profiling for chemical residues

Results from depth profiling (Figure 74) indicated that the levels of soluble pollutants in the sandstone were relatively low. Only the sulphate residues showed any indication of concentration of pollutants towards the outside of the stone, although the amount of sulphate present was not particularly high. Soluble sulphate levels declined from approx. 65 μg/g in the outer 4 mm to approx. 30 μg/g at 20 mm depth. Levels of chloride, sodium, fluoride and nitrate were also relatively low. Levels of phosphate were below the level of detection (20 μg/g).

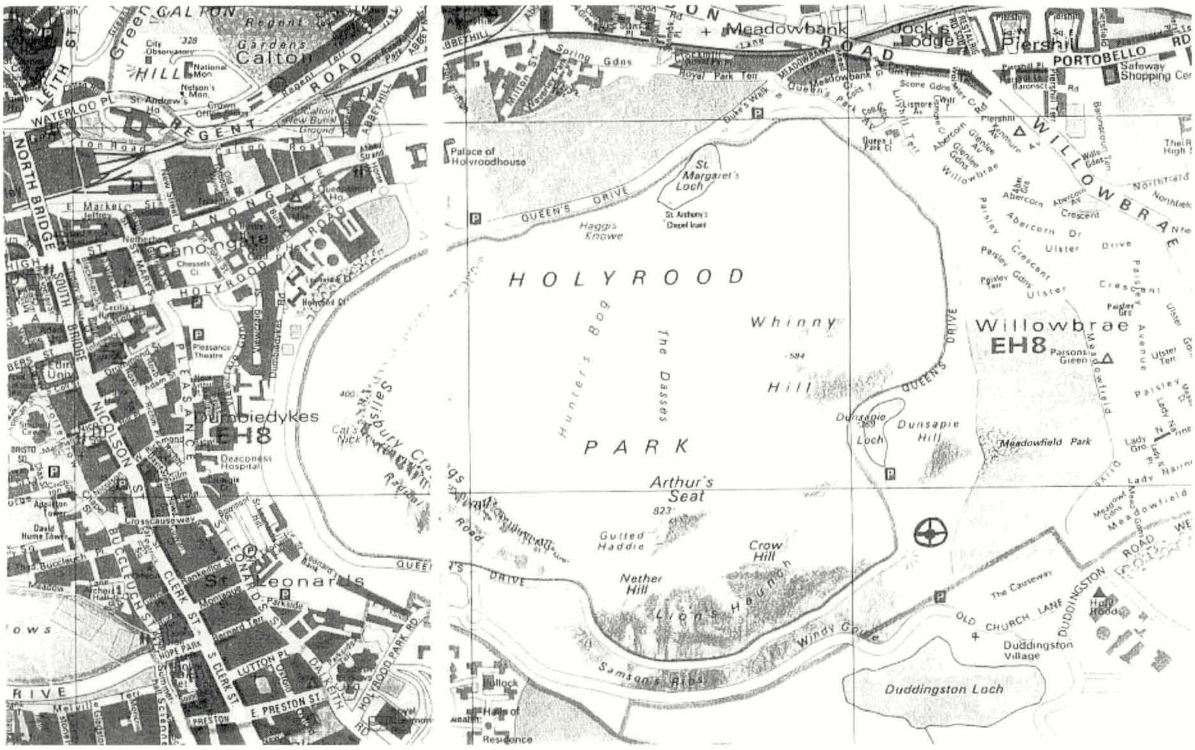


Figure 70 *Location of test panel at Holyrood Park.*
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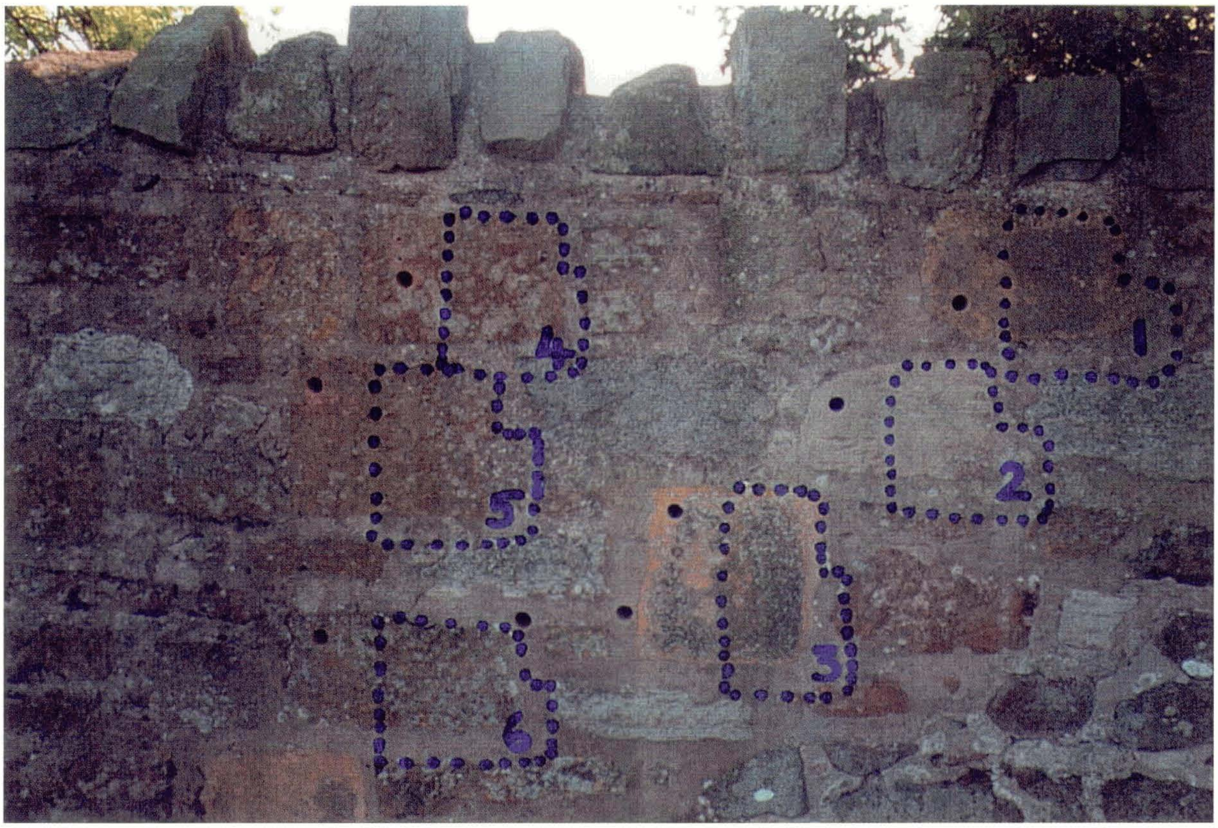

Figure 71 *Area of test panel at Holyrood Park.*

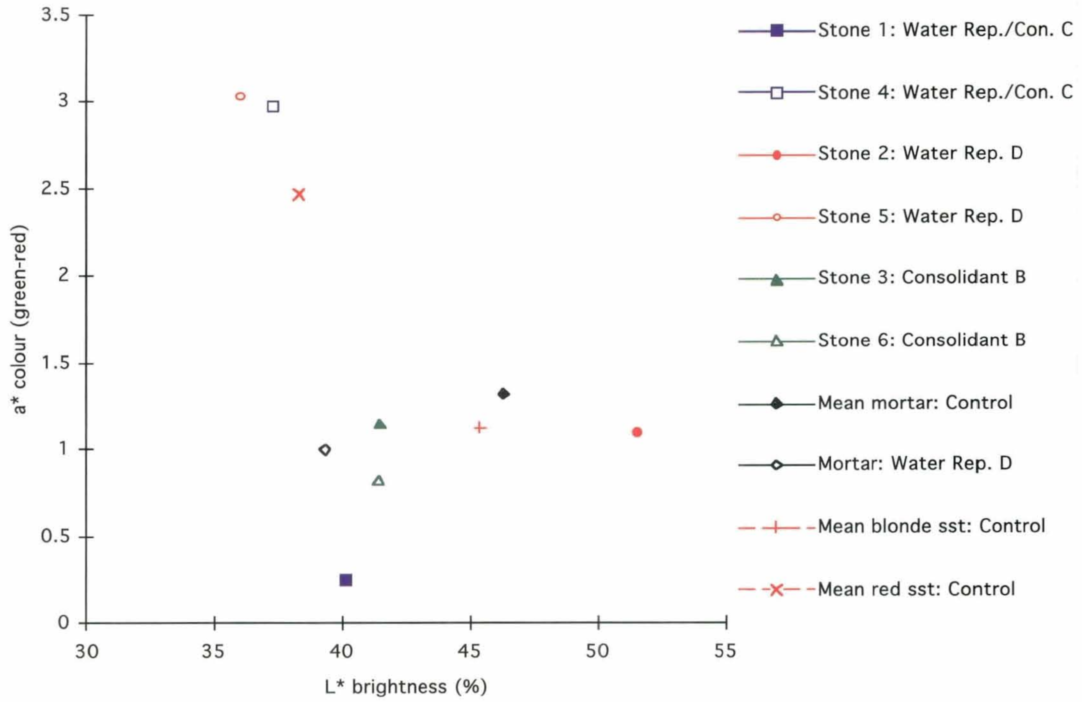

Figure 72 *Colour analysis of test panel sandstones before application of consolidants and water repellents.*

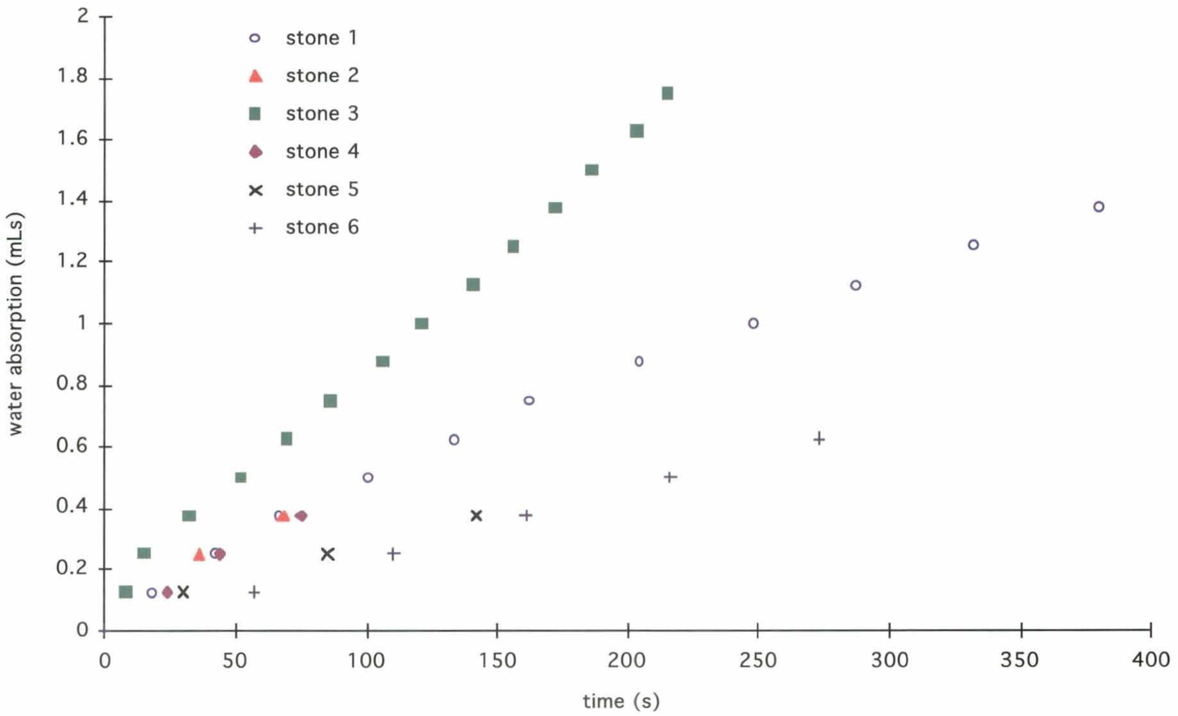

Figure 73 *Water absorption rate analysis of test panel sandstones before application of consolidants and water repellents.*

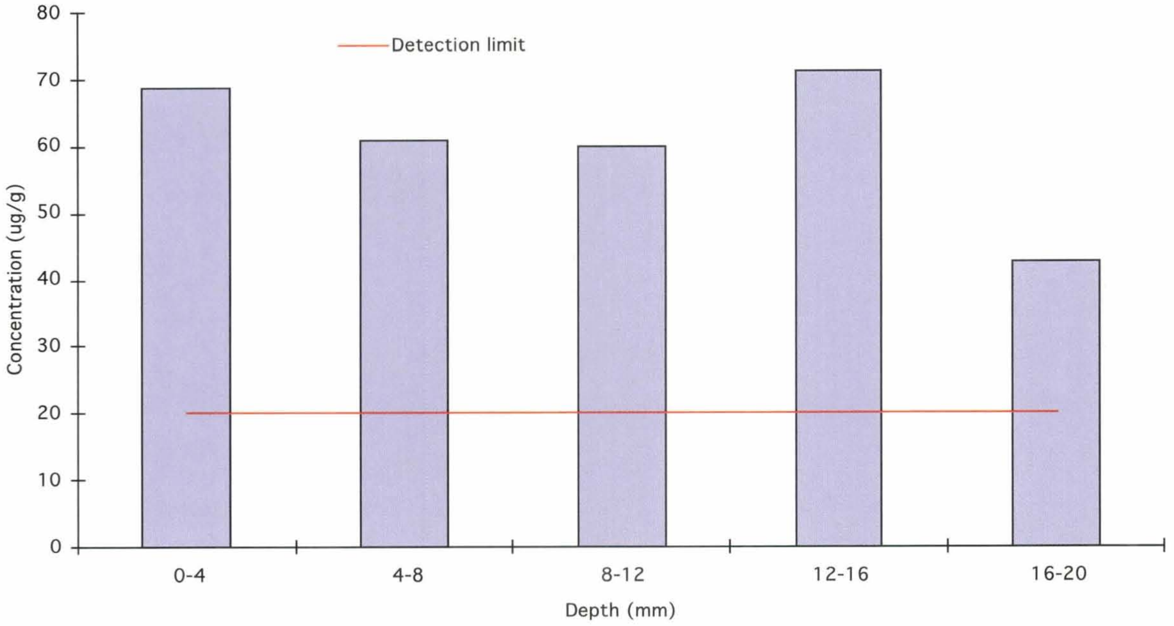

Figure 74a Results of depth profiling of sandstone block 4 at Holyrood Park for soluble chloride.

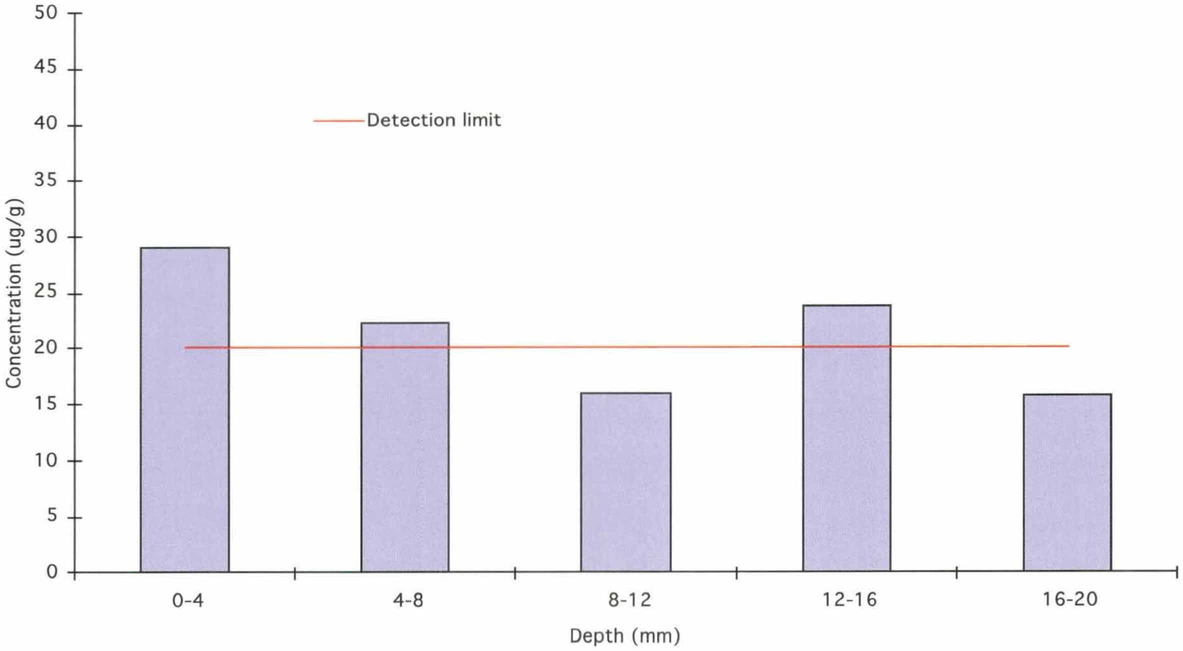

Figure 74b Results of depth profiling of sandstone block 4 at Holyrood Park for soluble nitrate.

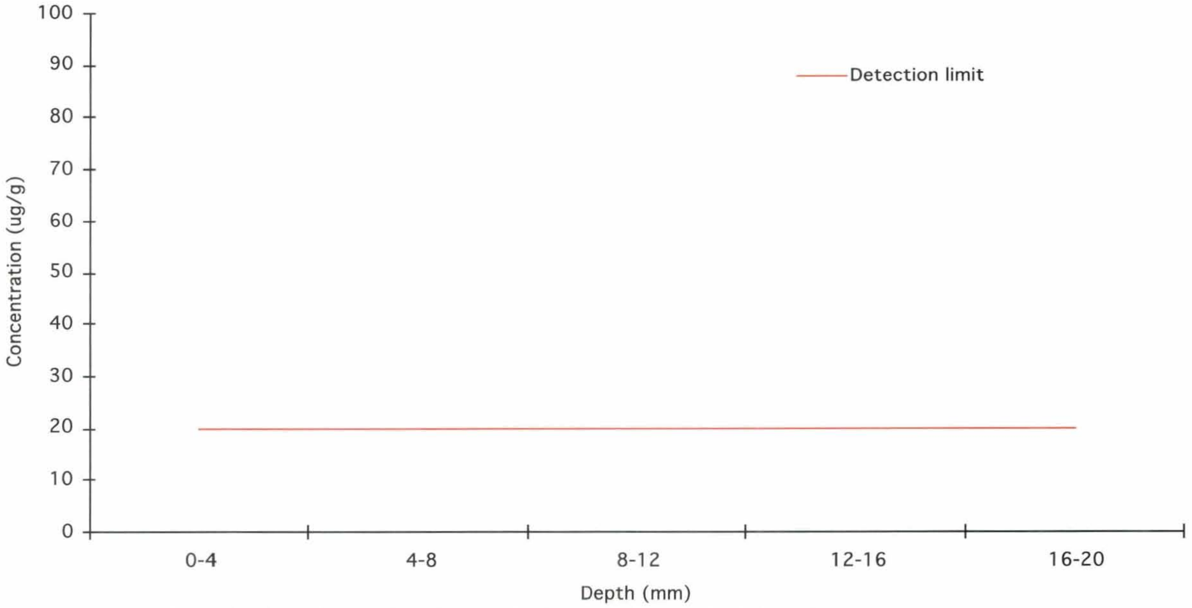

Figure 74c Results of depth profiling of sandstone block 4 at Holyrood Park for soluble phosphate.

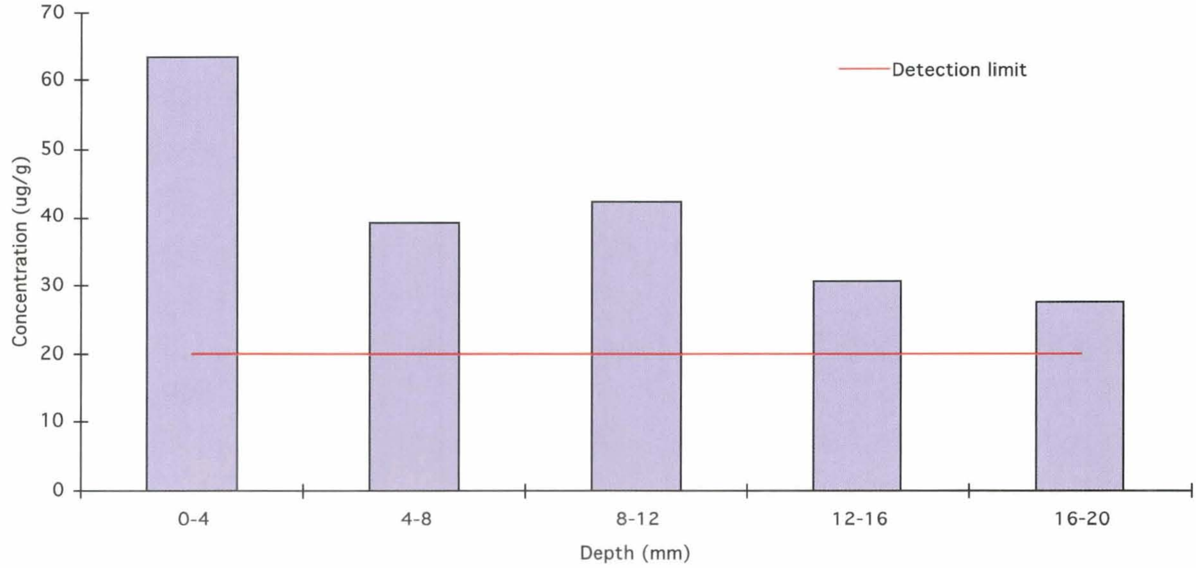

Figure 74d Results of depth profiling of sandstone block 4 at Holyrood Park for soluble sulphate.

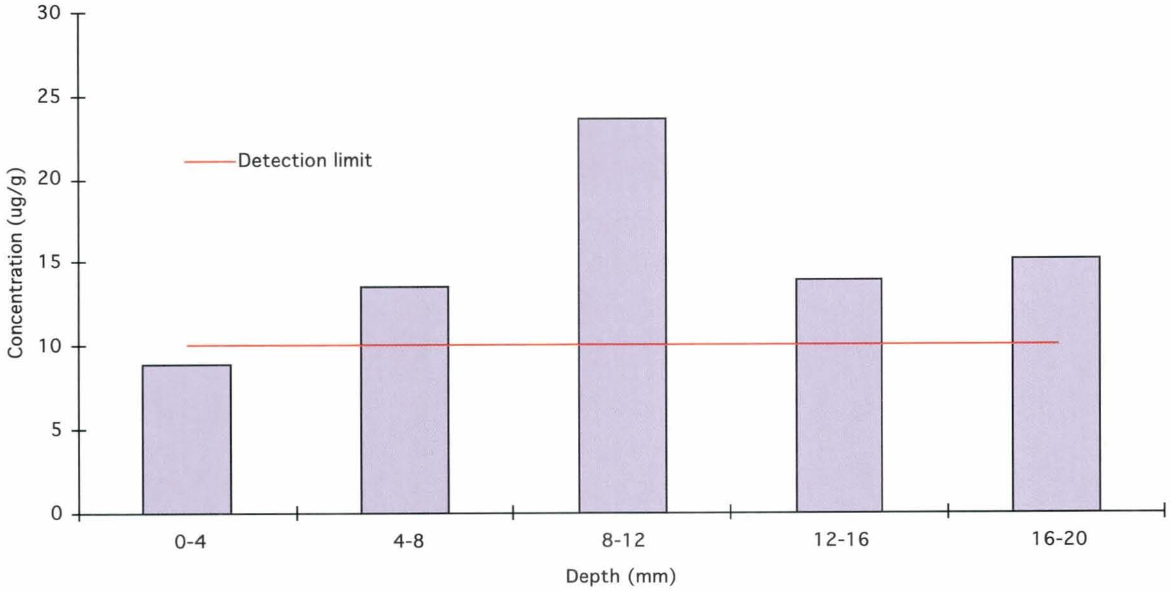

Figure 74e Results of depth profiling of sandstone block 4 at Holyrood Park for soluble fluoride.

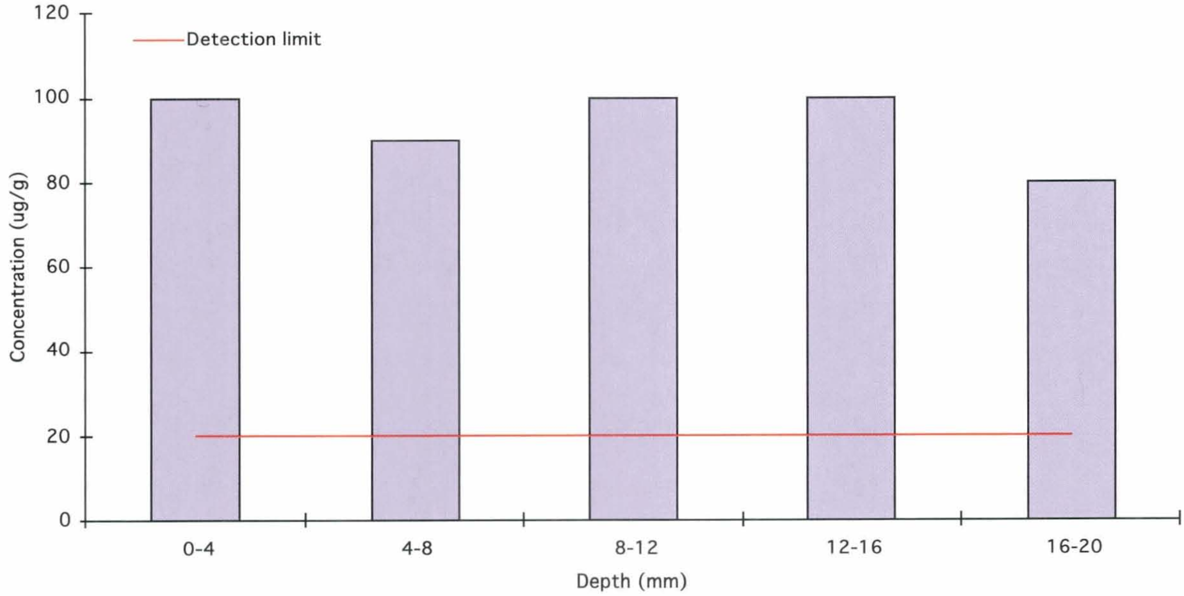

Figure 74f Results of depth profiling of sandstone block 4 at Holyrood Park for soluble sodium.

7 ANALYSIS OF RESULTS

This section draws together the results presented in previous sections showing correlations and inconsistencies between different data sets and summarises the conclusions that can be drawn from the data.

7.1 Colour changes

Surface rinsing with solvents after treatment is often recommended in application instructions for consolidants and water repellent agents. This should have the effect of removing surface residues and so reducing appearance changes. However, despite washing down the sandstone surfaces with solvents after treatment (for Consolidant A, Consolidant B and Water Rep./Con. C treatments), colour and brightness changes were still observed on all sandstone types at both the RGU (Section 4.4.1) and BRE (Section 4.1.2) test sites. The main colour changes noted were darkening of the surfaces. All four treatments caused colour changes which persisted for at least 1.5 years. Although effects could vary, on average the order of intensity of colour change observed on the RGU test panels was:

Consolidant B (most) ➔ Con. A ➔ Water Rep./Con. C ➔ Water Rep. D (least).

For the test panels at Myers Hill, where weather conditions were more severe than those encountered at the Aberdeen (RGU) test site, it was observed that the treatments could cause a white, patchy effect to develop under some weather conditions. This was probably a water related effect with sub-surface water passing out of the stone or dew and humidity condensing on the surface. The different porosity and hydrophobicity produced by the treatments may cause this. The patchy effect was not permanent, but would be a serious problem on ashlar or decorative masonry features if it appeared regularly. Surface rinsing with solvents after treatment can probably reduce or eliminate this effect.

Analysis of colour change data from the Aberdeen test site indicated that:

- Colour changes caused by consolidant or water repellent applications are greatest immediately after application and become reduced over time. Colour changes following treatment may be reduced as a result of:

  - abrasive effects of water washing and brushing (to removed debris from coring of blocks),

  - further maturation of the polymers in the sandstone,

  - degradation of polymers by sunlight,

  - degradation by moisture or oxidation,

  - biodegradation.

However, the stone colour is unlikely to return to its appearance prior to treatment application.

- 1.5 years after treatment Consolidant A and Consolidant B treated surfaces remained darker than comparable untreated surfaces.
- Treatment with Water Rep./Con. C and Water Repellent D appeared to reduce the rate of darkening of surfaces due to soiling accumulation relative to comparable untreated surfaces suggesting that there was a reduction in the soiling rate on water repellent surfaces.
- Consolidant and water repellent treatment on most sandstones caused increased red and yellow coloration. Effects varied depending on the original sandstone colour, but pale sandstones can be vulnerable to relatively large colour changes on treatment which are visible to the naked eye.
- Consolidant and water repellent treatments could cause colour changes which made the sandstone appear wet or damp even when completely dry. The degree of this appearance change varied between treatments and was greatest where two consecutive treatments (e.g. Consolidant A plus Consolidant B) were applied to the sandstone.

- Consolidant and water repellent treatments reduced the degree of colour change of sandstones on wetting - the more water repellent the treatment, the less the degree of colour change on wetting. This effect was due to the water repellents preventing or reducing water penetration of the surface.
- On initially soiled stones, consolidant or water repellent treatment can result in some removal of soiling (mainly during the solvent washing stage) which may mask any measurement of inherent colour change.

7.2 Water absorption and repellency and moisture movement

7.2.1 Liquid water absorption

In general the water absorption rates of sandstones (Section 4.4.2) were found to be slower after treatment with consolidants and water repellents. However, in some cases (Stainton [Water Repellent D & Consolidant B], Locharbriggs soiled [Consolidant B], Cat Castle [Water Rep./Con. C], "Unknown B" [Consolidant A, Consolidant B, Water Rep./Con. C & Water Repellent D], "Unknown C" [Consolidant B & Water Rep./Con. C], "Unknown A" [Water Repellent D]) moisture absorption rates within the first few seconds were initially faster than their values prior to treatment although the rate soon slowed (normally within a few seconds) to be lower than the rate on untreated (control) sandstone. This may be caused by changes in the capillarity of the surface after treatment (although no large changes in pore size were noted in porosimetry results (Section 4.4.10)). It is possible that on sandstones exhibiting this behaviour some consolidant or water repellent treatments could actually increase the superficial water uptake rates during short, heavy rainfall events, although over a longer period the water uptake appears to be reduced. However, there was no evidence from measurements of colour change on wetting (Section 4.4.1.2) that these samples showed any increased darkening (indicative of greater water uptake) relative to other similar sandstones.

On the "Unknown A" sandstone, some treatments (Consolidant A, Consolidant B & Water Rep./Con. C) resulted in an increase in the speed and amount of water taken up by the stone. This sandstone was highly soiled and initially had a particularly slow water absorption rate. It is likely that soiling removed by the solvents in treatments was responsible for increased water absorption. This would suggest that, contrary to the intention, application of water repellents to highly soiled sandstone could actually increase water absorption. In support of this, it can be observed in Figure 28 that on "Unknown A" sandstone treated with Consolidant A, Consolidant B & Water Repellent D the colour change on wetting indicated that this sandstone had taken up more water than the untreated sandstone.

Some sandstones (e.g. Clashach) can vary widely in moisture absorption rates. This may cause variations in absorption of consolidants and water repellents between sandstones and even within a single sandstone. Indeed, variation in consolidant and water repellent up-take was noted in the variation in amount of consolidant absorbed (Section 4.2.1) and in the depth of penetration measured on some sandstones (Section 4.4.4).

The treatments tested varied in their water repellency. Consolidant A is a consolidant with minimal water repellent properties and on some stone (e.g. freshly cut Locharbriggs and Clashach) it had a noticeably lesser effect on moisture absorption rates than other treatments. On some sandstones treated with Consolidant A (e.g. freshly cut Locharbriggs and Clashach) water absorption rates were initially slow becoming faster later on in the experiment. This suggests that after the surface has been wetted for some time the water repellency "breaks down". On the initially soiled sandstones Consolidant A appeared to be no less effective in terms of its effects on moisture absorption rates than any other treatment. The reason for this difference in behaviour between soiled and fresh sandstone is unclear. An apparent, transient water repellency effect with Consolidant A was also noted during experiments with water droplet and wetting/drying tests for depth of penetration (Section 4.4.4). A similar mechanism may therefore be responsible for both slightly water repellent effects.

7.2.2 Water repellency

Many consolidant or water repellent treatments cause increased hydrophobicity (water repellency) of substrates. Water is therefore a useful method of detecting the existence or location of treatments. For water repellent treatments, testing involving measurement of water droplet absorption time has been found to be a useful method for determining the depth of penetration of treatments. However, in tests conducted over several months it has been found that at least one of the consolidants tested (Consolidant A) changes its degree of water repellency during curing (Section 4.4.4.2). This is thought to be due to separation of hydrophobic and hydrophilic components of the consolidant during solvent evaporation.

For water repellent treatments, simply wetting core samples can reveal the depth of penetration of treatments as the treated area dries more rapidly than the untreated area and the treatment depth shows up as a change in colour. Results were made more visible if flat cut surfaces were used although the effect was also visible on the curved sides of cores. However, estimates of treatment penetration by wetting and drying were not the same as those obtained from measurements of water droplet absorption time, sometimes giving higher values and sometimes lower (Section 4.4.4). Silane based vapours were emitted from the samples for a period after treatment. The transfer of vapour deeper into untreated porous stone could further alter the water hydrophobic properties of the stone. As a result, deep depths of penetration obtained from water based tests could be detecting the paths of silane vapours and not applied, active consolidant.

7.2.3 Water vapour permeability

Consolidants may be designed with hydrophilic or hydrophobic properties depending on the required use. However, a desirable characteristic of such treatments is that they still allow water vapour to pass in and out of the stone surface. Ideally any stone treatment would not reduce the vapour permeability, however in practice this is unlikely to be the case. Preferably, for any treatment that does reduce the vapour permeability, the drop would be evenly placed through the treated stone. This is because a very sharp decrease in permeability near the surface of the masonry would cause a gradient which could attract subsurface crystallisation of salts and accelerate decay processes.

Water vapour permeability was found to vary widely between sandstones. Locharbriggs sandstone was the most permeable, being 10 times more permeable than Leoch sandstone (note that the difference in porosity was only about 3 times (Section 4.4.10). In general, water vapour permeability was increasingly reduced with increasing treatment, that is, towards the surface of treated sandstones. Assuming the results of water vapour permeability were due to the treatments and not to weathering or other natural changes in the stone, the following observations can be made:

- All four treatments tested reduced water vapour permeability on Locharbriggs, "Unknown B", Stainton and Clashach sandstones, but not Leoch.
- Where Consolidant A and Water Rep./Con. C reduced water vapour permeability this generally occurred at a depth up to 20 mm.
- Where Consolidant B and Water Repellent D reduced water vapour permeability this generally occurred at a depth up to 10 mm.
- The sharpest gradient of decrease in water vapour permeability occurred with Consolidant B on Locharbriggs with a difference of 20-30% between the underlying stone and the surface.

7.3 Strength tests

The results of these tests should be assessed in the context of the application method. This is because samples treated in the laboratory will be different from real buildings. Laboratory samples can be almost vitrified in treatment if the samples were to be held in consolidant during curing. This would obviously affect the strength properties of stone. However, in treatment of panels or buildings the treatment has an opportunity to soak or evaporate to other parts of the stone and atmosphere. The remaining consolidant is more difficult to detect using mechanical methods. All the strength tests for this project were carried out on samples that had been treated in detailed simulations of real buildings and using real application methods.

Consolidant A treatment appeared to show some consolidative effect on some sandstones between about 5-15 mm depth and Consolidant B also increased both the ultimate strength and the modulus of elasticity at up to 7 mm depth in some stone types. However, no consolidative effect was observed for Water Rep./Con. C or Water Repellent D (which is not intended to have a consolidative effect).

Treatment with Consolidant B increased the surface strength of sandstone, but this did not occur to any great depth. This consolidation effect occurs by the polymer holding together the stone. The other treatments appeared to give minimal or no structural increases in strength due to consolidation of the treated sandstones in test panels. However, none of the sandstones in the test panels (with the possible exception of soiled Leoch sandstone) was in a condition that would normally require consolidation. In the field sites there may have been evidence at the Arbroath site (where there was evidence of extensive stone decay) of some retention of the original treated face which was treated approximately 20 years previously (Section 5).

It is possible that consolidation of weathered surfaces could occur where siloxane vapour or consolidant inhibit the propagation of weathered cracks, and so the strength of the material increases in the weathered layers. This could be a mechanism of reversing structural decay in weathered surface layers. This type of consolidation could occur, but there was no strong evidence.

The effects of rinsing of the surface with solvents following treatment could significantly affect consolidation of a stone surface. Treatments may be rinsed out of the surface, or diluted by being pushed deeper into the surface, both of which will reduce the consolidation effect.

7.4 Exposure tests

7.4.1 Accelerated UV tests

For some sandstones, Consolidant B treated surfaces became lighter in colour due to UV exposure. The original treatment has been shown to darken the surfaces and it may be that the appearance change is a return to the original colour of the stone.

Some Water Rep./Con. C treated soiled sandstones became substantially lighter, almost bleached. As no other samples appeared to show bleaching of weathered surfaces, it would appear that a specific effect involving both the soiling and the Water Rep./Con. C has occurred, but it is unclear exactly what.

Due to the very simple and artificial nature of UV accelerated tests, only long term real exposure tests would enable further analysis of the risk of colour changes.

7.4.2 Freeze-thaw tests

During and after the test no frost damage to treated areas was observed on any sample, although untreated parts of the samples did sustain some damage. The treatments did not appear to increase the frost susceptibility of the sandstones. Results of mercury porosimetry (Section 4.4.10) would also suggest no increased susceptibility to frost damage since no increase was found in microporosity (which can increase frost sensitivity). However, it is possible that hydrophobic treatments may still increase frost damage in the field as any barrier which can trap water behind the surfaces may make the stone underneath subject to more aggressive frost effects.

7.5 Dilatometry

Consolidants and water repellents may cause stone masonry to expand or contract. If this occurred over a large area it could result in cracking and delamination. The significance of the dimension changes that have been found in laboratory tests are difficult to quantify. Results show overall size changes of the order of 0.1% which is essentially very "small". However, water wetting cycles alone have been shown to reduce the strength of some porous masonry or to significantly alter the shape of stone cladding. Comparison of the dimensional changes of the consolidants due to the effect of water alone (i.e. the control sample) can therefore provide a relative guide. The following observations can be made:

- The dimension changes caused by Consolidant A, Consolidant B and Water Rep./Con. C were all significantly larger than the effects of water.
- Dimension changes for Water Repellent D were comparable to the effects of water.
- All treatments caused a slight increase in the susceptibility to water related changes compared to the control.

The measurements taken from either side of the cores were not consistent and showed that the treatment could result in bends and curves as can happen with water wetting cycles in stone cladding. The existence of bedding planes, variations in porosity and uneven absorption of the consolidant could all cause this variation. The largest dimensional change was Consolidant B which reduced in size on one side of the core by 0.14%. This would correlate to a 1.5 mm reduction in size across an area one metre wide.

7.6 Emission of volatile organic compounds

Volatile organic compounds (VOCs) are released during the curing of solvent based consolidants and water repellents. Initial VOC losses were mostly caused by loss of the solvents used as a transport vehicle and reaction medium. There are a range of other sources of volatile compounds:

- the consolidant monomers
- partially polymerised monomers
- condensation products from reactions (e.g. water, alcohol, acetone, methanol, etc.)
- re-evaporation of absorbed atmospheric moisture or chemicals

All the treatments tested initially emitted VOCs which would require appropriate breathing apparatus for application and periods of time afterwards. The VOCs produced will depend on the type of consolidant or water repellent used. In these tests compounds detected included alcohol, acetone, butan-1-ol, methyl ethyl ketone, white spirit, toluene, xylene, all of which are solvents. Consolidant compounds detected included silanol and siloxane. In tests which simulated a vertical wall application, the majority of solvent evaporated over a period of 20-100 hours. After 100 hours some VOCs were still detected. In outside environments these would not constitute a major fire hazard, but should still be treated with care. If, for example, plastic sheeting is used to cover the treated area build-ups of treatment could occur behind the sheeting. For silica-bearing consolidants and water repellents organic silica compounds may be emitted for some time after treatment, possibly until cross polymerisation or setting is complete.

The loss of consolidant monomer and partially polymerised monomer is likely to be particularly important as this will result in loss of consolidant which may reduce the level of consolidation. Consolidant monomers and partially polymerised monomers may evaporate and condense in other parts of porous stone, affecting its hydrophobic or hydrophillic properties.

Curing of consolidants appears to have two phases. An initial drying and curing over a period of 20-100 hours which results in the loss of a substantial amount of the original solvents, and some evaporation of actual consolidant. Subsequently there is a slow even loss of solvent and possibly consolidant monomer or polymer over a period of about two months or more.

For sample prisms (50 x 50 x 15 mm) which had been soaked in various solvents (toluene or white spirit) or consolidant or water repellent treatments (Consolidant B, Water Rep./Con. C and Water Repellent D) the fastest rate of solvent loss was found for toluene treatment alone, solvent loss being completed in about 8 days. Loss of toluene from samples treated with a toluene based consolidant (Consolidant B) was somewhat slower taking up to 20 days, presumably due to porosity reduction in the treated samples and perhaps because the consolidant itself retained the solvent for longer. Loss of butanone (methyl ethyl ketone) and toluene from Water Rep./Con. C treatment took up to 24 days (the rate of pure solvent evaporation was not measured since insufficient samples were available). By far the slowest solvent losses were from samples treated with white spirit or the Water Repellent D, which uses white spirit as a solvent. Evaporation of white spirit alone could take up to 92 days, for Water Repellent D treated samples evaporation could take up to 183 days. Clearly, the rate of solvent loss from treated substrates can vary widely depending on the solvent used and the amount of treatment taken up by the substrate. Results show (Section 4.4.8.3) that more porous substrates take up more treatment and take longer to lose volatile solvents than less porous substrates.

7.6.1 Treatment residues following loss of VOCs

Following loss of VOCs the amount of treatment residue in samples was found to be:

38% of Consolidant A,

8-12% of Consolidant B,

35-40% of Water Rep./Con. C, and

3-8% of Water Repellent D

The majority of lost volume is from solvents used as carriers for the treatment. However, some volatile compounds may be lost from the consolidant or water repellent, especially if polymerisation is delayed.

7.6.2 Solvent evaporation from sandstone and mortar

In experiments with treated sample prisms of sandstone and mortar, substrates with higher porosity were generally found to take up more of the applied treatment. These more porous substrates also took longer to lose solvents. This is likely to be due both to the larger volume initially taken up and possibly to deeper penetration of the treatment.

For silane based consolidants slightly more consolidant may be retained in siliceous substrates than in calcareous substrates since the presence of calcite in a stone retards the polymerisation reaction and may allow significant quantities of silane to evaporate before polymerisation can occur (Section 2.2.3.1).

The depth of penetration of treatments is likely to affect evaporation rates of solvents and monomers. Solvents will all eventually be lost from the substrate. However, where the depth of penetration is relatively high it is more likely that the monomers in silane based treatments will be retained for long enough for most to become polymerised. Where the treatment penetration is low, there may be significant evaporation of unpolymerised consolidant monomers. For Water Rep./Cons. C the amount of consolidant retained in the 1:1:6 mortar samples was relatively low compared to the other substrates (Section 4.4.8.3). In experiments measuring the depth of penetration 1:1:6 mortar was found to have the smallest penetration of the three mortars assessed (Section 4.5) and it also had the lowest initial uptake of consolidant/water repellent/solvent in experiments to measure rate of solvent loss (Table 14). For consolidants or water repellents where unpolymerised treatment materials may be lost by evaporation it therefore seems that where relatively little treatment is taken up and where penetration depth is low, a significant proportion of the treatment may be lost through evaporation.

Loss of unpolymerised treatment may be a safety concern since many consolidant or water repellent treatments contain silane monomers which are extremely hazardous to health, being damaging to both eyes and lungs. Where polymerisation is slower or evaporation rates higher this will result in a greater concentration of these harmful chemicals in the atmosphere.

7.6.3 Hazards and health and safety

The existence of volatile silica containing compounds should be considered a hazard. These do not necessarily constitute organic compounds but are organo-silica based compounds which may require different health and safety procedures.

All treatments emitted compounds which should be considered flammable and require suitable breathing apparatus and protective clothing when being used. However, after treatment it may be difficult to determine exactly when the health and fire risks have reduced. In exposed locations the fumes probably diffuse away quickly. In enclosed areas the fumes may remain for several days. Manufacturers' instructions for some of the products recommend sealing treated surfaces with foil or plastic to contain the solvents and consolidants vapours for up to two weeks. When treated surfaces are sealed in this way the areas contained may be highly flammable and still pose health risks.

7.7 Mercury porosimetry

7.7.1 Sandstones

Of the four consolidants and water repellents tested, none were found to completely block porosity in the sandstones. Where loss of porosity was found following treatment this was generally small relative to the total porosity of the sandstone. In the sandstones tested, total effective sandstone porosity ranges from about 7-25%. The treatment that resulted in most porosity reduction (Consolidant A) resulted, on average, in a 3% loss in porosity in the more porous sandstones. Consolidant B reduced porosity by about 1.4% and for Water Rep./Con. C and Water Repellent D results indicated an average of less than 1% loss of porosity. Therefore, while Water Rep./Con. C and Water Repellent D had little overall effect on total porosity, treatment with Consolidant A and, to a lesser extent, Consolidant B, did appear to result in a some reduction in porosity although the results were not statistically highly significant. A reduction in surface porosity caused by a consolidant treatment could be a problem if it resulted in substantially reduced evaporation rates for treated sandstones, as increased time of wetness can increase the rate of deterioration of the sandstone. While results from determination of water vapour permeability did indicate some reduction in treated sandstones, the degree of permeability reduction was not thought to be excessive (Section 4.4.5).

Examination of changes within particular pore size ranges indicated that most losses in porosity were for pore sizes in the 100-10 μm range, though results varied depending on sandstone type. There was little evidence of any increases in porosity at the <5 μm range indicating that treatments should not result in any significantly increased vulnerability to frost damage. Indeed, freeze-thaw testing did not find any increased vulnerability to frost damage in treated sandstones (Section 4.4.62).

7.7.2 Mortars

Due to the variability in porosity of mortars, mercury porosimetry was unable to determine any significant differences in porosity between treated and untreated mortars.

7.8 Consolidant and water repellent treatment of mortars

The penetration of water repellent treatments into mortars varied depending on the durability of the mortar mix, penetration generally being greatest in the least durable mortars. The deepest penetration was found in lime mortar (up to approx. 80 mm), moderate penetration was found in the 1:3:12 mix mortar (up to approx. 40 mm) and the least penetration was found in the 1:1:6 mix mortar (up to approx. 30 mm). For the least durable mortars water repellent penetration could be greater than in many sandstones, but for the most durable mortars depth penetration was often found to be lower than in sandstone.

Where the mortar-sandstone joint is cracked, it is possible for water repellent to "track in " along the joint (especially along upper edges of sandstone blocks) allowing deeper penetration of the water repellent than could occur in the bulk mortar or sandstone. This effect is most likely to occur when recessed mortar sits over projecting sandstone, where the treatment can pool when applied.

Measurement of the depth of penetration of water repellents in joint mortar and in mortar test cubes showed that results were not directly comparable. Although the method of application for the treatments was the same for the test panels and the mortar cubes (the mortar cubes were attached to the test panels and were treated at the same time), the measured depths of penetration differed. In some cases (e.g. lime mortar) penetration in the test cubes was markedly lower than in joint mortar. This effect is thought to result from differences in the density of mortar in the joints and cubes which could result from differential compaction and from the effects of mortar bulk on setting, curing and weathering. Whatever the origin of these differences, these results indicate that tests on water repellent penetration into bulk mortar samples will not give a reliable indication of the likely penetration in joint mortar.

The effects of porosity in mortar and sandstone differ with respect to depth of penetration of water repellents. This may be caused by differences in the chemical composition of the materials, mortars being relatively rich in calcium oxides/carbonates and sandstones being rich in silicates. Differences in pore size distribution or in pore shape or continuity could also have an effect.

The long term effects of water repellents when applied to mortar are unclear. However, it has been shown that the deepest penetration of water repellent occurred in the least durable mortar mixes and that penetration was often greater than that in sandstones. It is possible that in such situations water repellents could reverse the normal pattern of moisture loss in a wall, allowing more moisture evaporation through the stone rather than through the mortar (especially since water repellents have been shown to be drawn into cracks at joints relatively deeply when compared to the stone). However, since the water repellent will prevent normal evaporation of trapped moisture at or close to the wall surface the long term consequences are difficult to predict.

7.9 Chemical cleaning of treated sandstone

There was little difference between Water Rep./Con. C and Water Repellent D in the colour changes they caused on treated, cleaned sandstones and with respect to how they affected absorption of applied chemical cleaning agents (Section 4.6).

Both treatments caused darkening of the sandstone (see also Section 4.4.1) and some increased red and yellow coloration. Chemical cleaning of treated samples resulted in some return in brightness, although it did not normally restore brightness to its pre-treatment level. Chemical cleaning alone often caused substantial increases in red and yellow coloration. Similar increases in coloration were noted on previously treated sandstones. Treatment with either Water Rep./Con. C or Water Repellent D does not therefore result in any extreme colour changes on chemical cleaning, beyond those which would be predicted from either the treatments or the chemical cleaning alone.

Treatment with either Water Rep./Con. C or Water Repellent D substantially reduced the levels of residual stonecleaning chemicals in the sandstones. Increased soluble sodium levels resulted from residues of the alkaline cleaning agent. Increased soluble fluoride and phosphate originated from the acidic cleaning agent.

While residual chemicals in untreated sandstones could often be found to over 20 mm depth, in sandstones with either water repellent treatment, residual chemicals were found mainly in the outer 0-2 mm, occasionally to 5 mm depth. There was no noticeable effect on levels of sulphate, chloride or nitrate and there was no evidence that either treatment has resulted in the introduction of any of the examined ions (sodium, fluoride, phosphate, sulphate, chloride or nitrate) into the sandstones.

There was some suggestion that (for porous sandstone types) chemical residues were slightly higher in the Water Rep./Con. C treated samples compared to samples treated with Water Repellent D. This effect may be due to the greater water repellency of the Water Repellent D treatment but the results were not statistically significant.

These results appear to indicate that chemical cleaning carried out on water repellent treated sandstone should be less potentially damaging than cleaning carried out on untreated sandstone. However, it should be noted that these data were taken from sandstone samples within a few weeks of cleaning. The effects of water repellents and consolidants with respect to the later redistribution of soluble salts in the sandstone (as is likely to happen on buildings exposed to rainfall) is unknown. It is for instance possible that in stone exposed to weathering the chemical residues in treated sandstones might become concentrated at depth in the sandstone at the limit of penetration of the treatment. This could accelerate decay at depth in the stone leading to spalling of the surface.

7.10 Soiling rates with selected water repellents

Some water repellents were found to remain tacky for several months when applied to carbon disks. If these treatments remained tacky on a stone surface this could lead to increased soiling rates due to the attraction of dust particles onto the stone surface. However, when the soiling rates of tacky and non-tacky water repellent treated sandstones were compared over seven months, no increased soiling was observed on sandstones treated with the tacky water repellents.

7.11 Re-application of treatments

Consolidant B was applied as a subsequent treatment to test panels which had, one year previously, been treated with Consolidant A or with Water Repellent /Consolidant C. Re-application of this treatment caused further darkening of the sandstones. By the time of writing (approx. 12 months after application) no other deleterious effects had been noted.

7.12 Amount of consolidant or water repellent absorbed and depth of penetration

One of the most important considerations with respect to application of consolidants and water repellents is the amount of treatment taken up by the stone. A wide variety of tests has been used here to determine the amount of consolidant or water repellent taken up by the sandstones and the depth of penetration of the treatments.

7.12.1 Treatment absorption by sandstones

The amount applied to a stone or area can be calculated by weighing or measuring the volume of treatment that had been applied and dividing this by the surface area of the stone. (**NB** It should be remembered that the concentration of consolidant or water repellent in products can vary widely.) This calculation can be complicated by difficulties in preventing excessive run-off from the surface during application. In addition, the amount of treatment taken up can vary significantly between stone and mortar, between different stones and even across a single stone. Manufacturers' recommendations for many treatments specify that the surface should be washed down with solvent after application to prevent excessive colour changes due to consolidant material remaining on the surface. This will remove some consolidant from the surface and could result in significant loss of consolidant if the penetration depth is low (i.e. <5 mm). Under some circumstances, evaporation of unpolymerised monomers prior to their polymerisation may also result in significant losses of consolidant.

For one treatment (Consolidant B, Section 4.2.2) it was found that increasing the concentration of the consolidant, thereby increasing the viscosity of the mix, allowed for greater absorption of consolidant since the rate of run-off was slower.

However, despite the draw-backs, calculations of volume applied per unit area can give a useful indication of the amount of material taken up by the stone and may be used (in conjunction with other data – see below) to give an indication of the depth of penetration.

The amount of consolidant or water repellent taken up by a sandstone can vary widely. In the experiments described here the amount absorbed ranged from 173 g/m^2 for fresh Leoch sandstone (low porosity) to 3267 g/m^2 for fresh Locharbriggs sandstone (high porosity) a difference of about 20 times. Weathering and decay can increase the porosity of sandstones resulting in increased absorption of treatments relative to comparable fresh sandstone.

Results indicated that the presence of weathered surface layers did not inhibit penetration of treatments into sound stone beneath the friable surface. For water repellent treatments, compositional differences between bedding planes (e.g. in Locharbriggs sandstone) could, on some occasions, be observed to distort the absorption of treatments or cause tracking of the treatments (illus 77). Differences in colour on Locharbriggs sandstone treated with Consolidant B indicated that penetration of this acrylic-based consolidant did differ between bedding layers in the sandstone (Figure 13i).

7.12.2 Depth of penetration

Depth of penetration of treatments can be assessed by a range of techniques including structural tests, water permeability, water drop tests, wetting tests and tomography. However, each test will produce different results. Water repellent treatments and consolidants can be detected relatively easily using water based tests. However the hydrophilic Consolidant A was more difficult to detect as its water related effects changed over a period of several months after treatment. Areas that were still hydrophobic slowly altered to become hydrophilic on exposure to air. In addition when surfaces became hydrophilic on the surface, significant hydrophobic areas were still present below the surface more than 7 months after treatment, and showed little signs of vanishing. Over time, the tests became either inaccurate or ineffective as the hydrophobic nature of the treatment changed to hydrophilic. As a result in some circumstances the RILEM tests with water absorption can produce misleading results. The wetting and drying tests appeared to be better at consistently detecting hydrophilic consolidants visually. The depth of penetration of consolidants was only detectable in all samples and treatments by adopting a range of water based tests in addition to the RILEM tests.

Water vapour permeability tests at incremental depths could determine depths of penetration. Results for Consolidant A, Consolidant B and Water Rep./Con. C were consistent with general results from all the water based tests. It was difficult to detect a change in vapour permeability for Water Repellent D and so no depth of penetration could be determined for that treatment using this method.

Using tomography, a sample of Locharbriggs sandstone treated with Water Repellent/Consolidant C produced a depth of penetration consistent with other results.

	Consolidant A	**Consolidant B**	**Water Rep./Con. C**	**Water Rep. D**
Water drop and wetting tests		**X**	**X**	**X**
Water drying	**X**	**X**	**X**	
Water vapour permeability	**X**	**X**	**X**	
Tomography	**n/a**	**n/a**	**X**	**n/a**

n/a = No data available

Table 36 Suitability of tests for detection of consolidants and water repellents from cross comparison of data.

7.12.3 Prediction of depth of penetration

The depth of penetration of treatments has been determined by measuring the water repellency in the water droplet test (Section 4.4.4). If we compare this data with the amount of consolidant or water repellent taken up by the sandstones (Section 4.2.1) it can be seen that, especially for water repellent treatments, there was a relationship between depth of penetration and amount applied (Figure 75). This relationship would be expected as the more treatment is applied to a stone, the deeper it might be expected to penetrate. The relationship is not so clear for non-water repellent treatments (Consolidant A and Consolidant B) probably because the water droplet test is not such a good measure of the penetration of these treatments. The amount of consolidant or water repellent taken up by a sandstone may therefore be used as a rough predictor of the depth of penetration of the treatment, provided that a relationship has been established for that treatment.

Predicting depth of penetration from the amount of treatment taken up by the stone may be useful in practice if each stone can be assessed separately. However, if we wish to know in advance what the depth penetration is likely to be we need a predictor of penetration derived from some other measurable factor.

The porosity of sandstones affects how they take up consolidants and water repellents. Using data (Section 4.4.4) on the depth of penetration of water repellency in the samples as a measure of the depth of penetration of the consolidants and water repellents, it is possible to determine the relationship between depth of penetration of the treatment and the porosity of the sandstone (Figure 76). There was found to be a relationship between porosity and depth of penetration with more porous sandstones showing greater depth of penetration. The highest penetrations were achieved with Water Rep./Con. C and Water Repellent D. Consolidant B had only a very small penetration even on very porous sandstones.

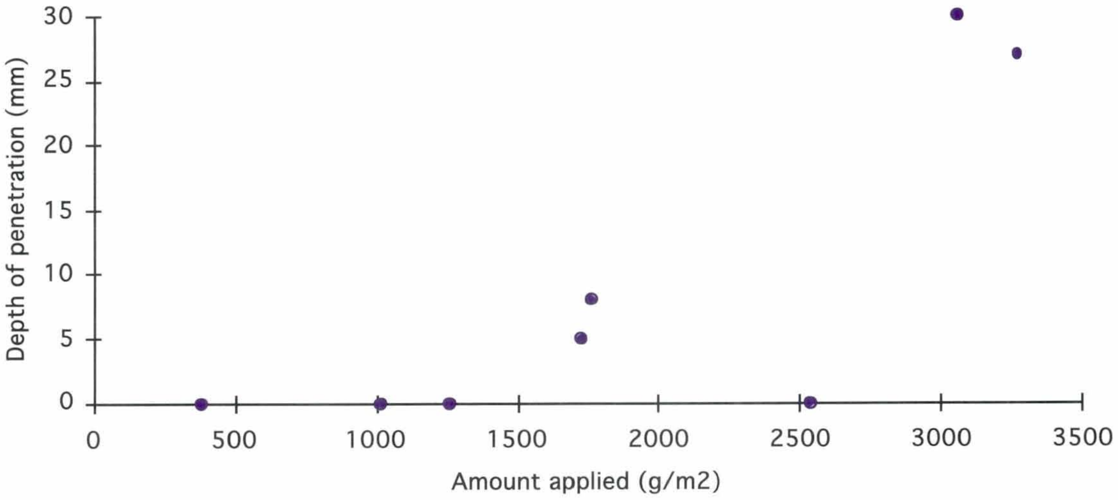

Figure 75a Correlation between depth of penetration and amount of consolidant or water repellent applied for Consolidant A.

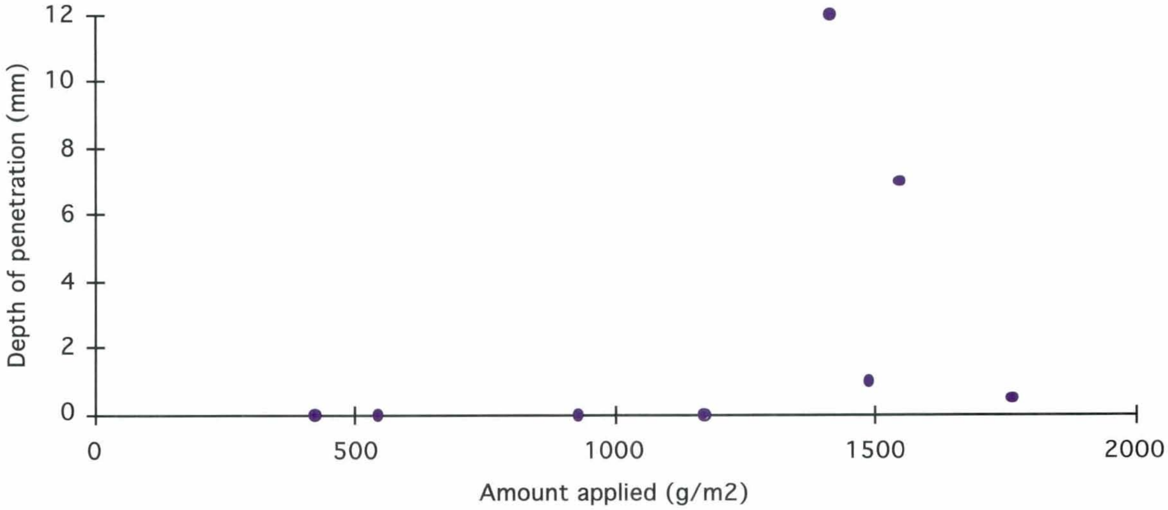

Figure 75b Correlation between depth of penetration and amount of consolidant or water repellent applied for Consolidant B.

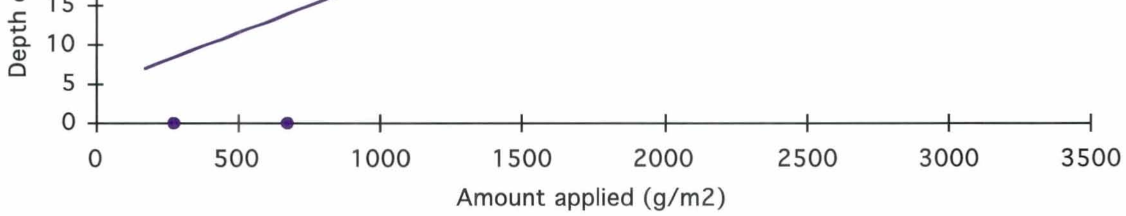

Figure 75c Correlation between depth of penetration and amount of consolidant or water repellent applied for Water Rep./Con. C.

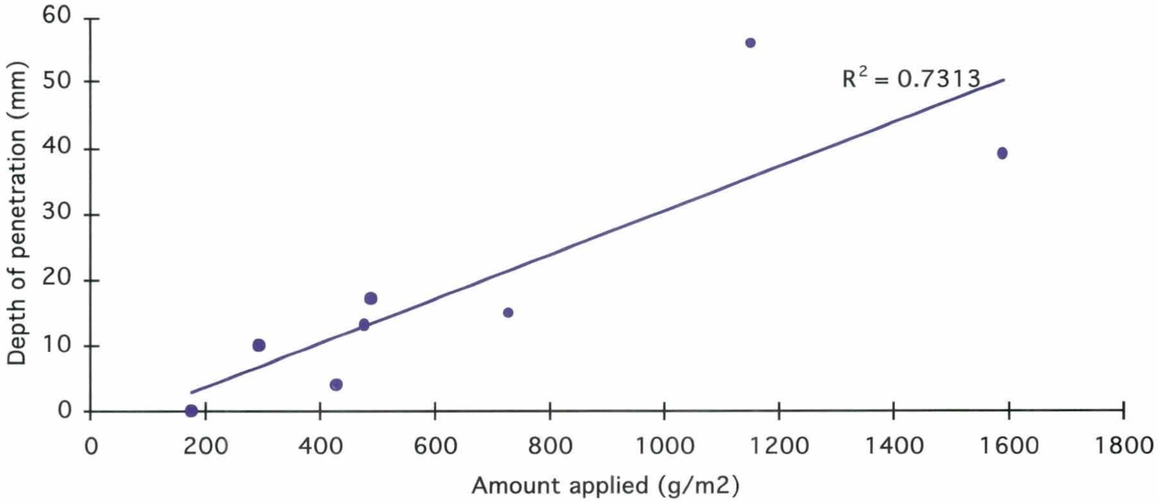

Figure 75d Correlation between depth of penetration and amount of consolidant or water repellent applied for Water Repellent D.

As a rough guide to penetration depth, Table 37 shows, for each of the treatments tested, what penetration depth might be expected given the sandstone porosity. These figures can be taken only as a very rough guide, since there was considerable spread in the data - standard errors were quite high (Table 37). For the Consolidant B treatment (as used here) no naturally occurring sandstone will have sufficient porosity to achieve even 10 mm penetration as few sandstones have even 25% porosity. Depth penetration of at least 20 mm should be easily achievable on most sandstones for Water Rep./Con. C and Water Repellent D and depths of about 10 mm should be achievable for Consolidant A.

Porosity (%)	**Water Rep./Con. C (±10 mm)**	**Water Rep. D (±15 mm)**	**Consolidant A (±10 mm)**	**Consolidant B (±4 mm)**
5	0	0	0	0
10	6	5	1	0
15	16	16	6	2
20	26	26	11	3
25	37	36	16	5
30	47	46	21	6

Table 37 Prediction of penetration depth (in mm) of treatments in sandstones depending on porosity. (Standard error shown in brackets).

Water absorption rates (Section 4.4.2) were obtained for all the sandstones in the test panels except Leoch where the water absorption rate was too low to give reliable results. Water absorption rate may be used to estimate the rate of absorption of applied consolidants or water repellents and may therefore allow an estimate of depth of penetration of the treatments.

Figure 78 shows the relationship between the water absorption rate of the sandstones and the amount of consolidant or water repellent taken up by the sandstone. There was found to be a relationship between the rate of water absorption and the amount of consolidant or water repellent it took up. Most treatments (all the treatments tested here) require that the material is applied to saturate the sandstone and more will therefore be required on more absorbent stones. Generally the more absorbent the sandstone the more consolidant it took up. However, when the water absorption rate and depth of penetration data was examined (Figure 79) there was found to be very little relationship between the two data sets. Figure 79 shows the relationship between amount of water absorbed in 300 seconds and the depth of penetration of a treatment. Only six data points were available for each treatment, but the data show that, with the exception of the Water Repellent D treatment, water absorption rate was not a good predictor of the depth of penetration of a treatment.

The penetration achieved by treatments depends not only on the chemical structure of the consolidant or water repellent but also on the solvent it is carried in. While these experiments have found Consolidant B carried in toluene (10% w/v) to have a very low penetration, use of other solvents or different concentrations might give deeper penetration. Where a 30% solution was used at Myers Hill (Section 4.2.2) better absorption of the consolidant was thought to be achieved.

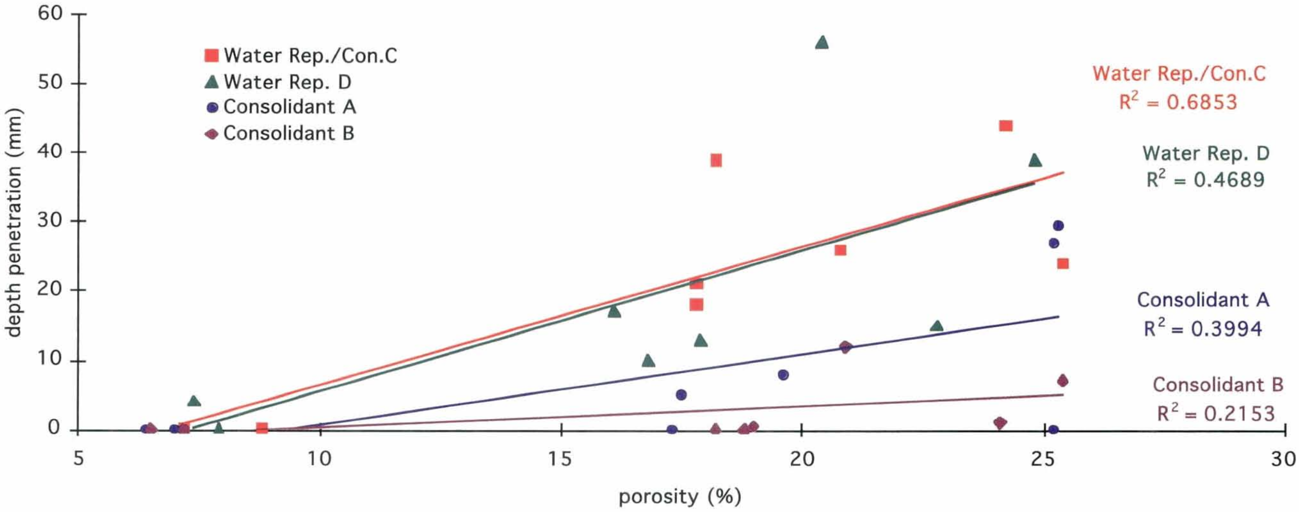

Figure 76 Correlation between sandstone porosity and depth of penetration of consolidants and water repellents.

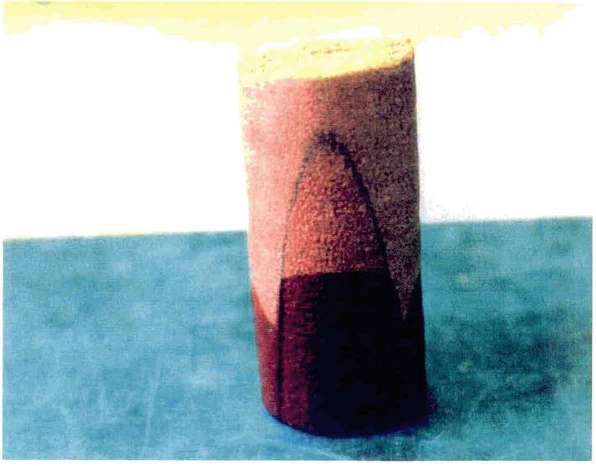

Figure 77 Water Repellent D tracking up along bedding plane in Locharbriggs sandstone.

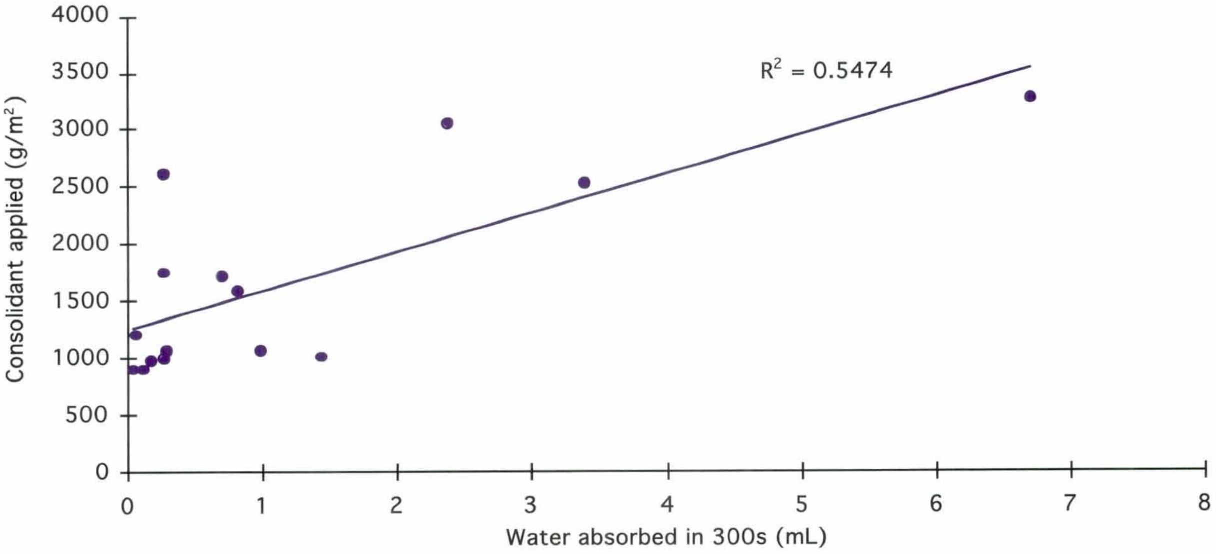

Figure 78a   Relationship between amount of Consolidant A taken up by a sandstone and the amount of water taken up by the stone in 300 seconds.

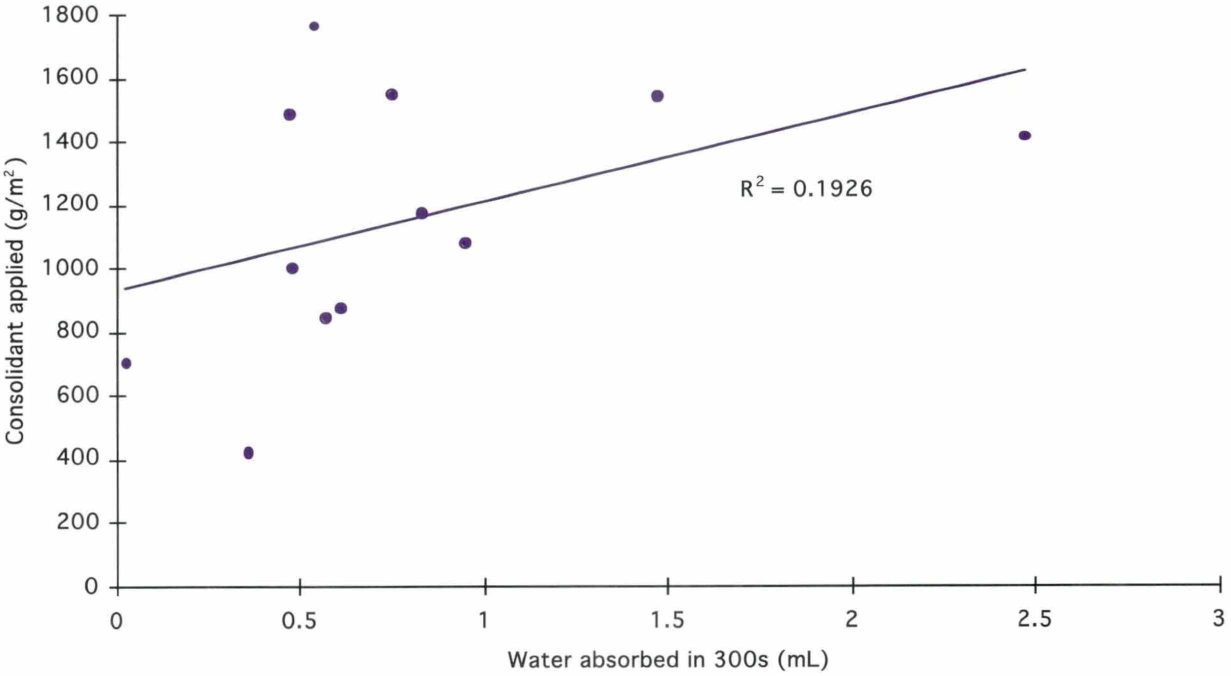

Figure 78b   Relationship between amount of Consolidant B taken up by a sandstone and the amount of water taken up by the stone in 300 seconds.

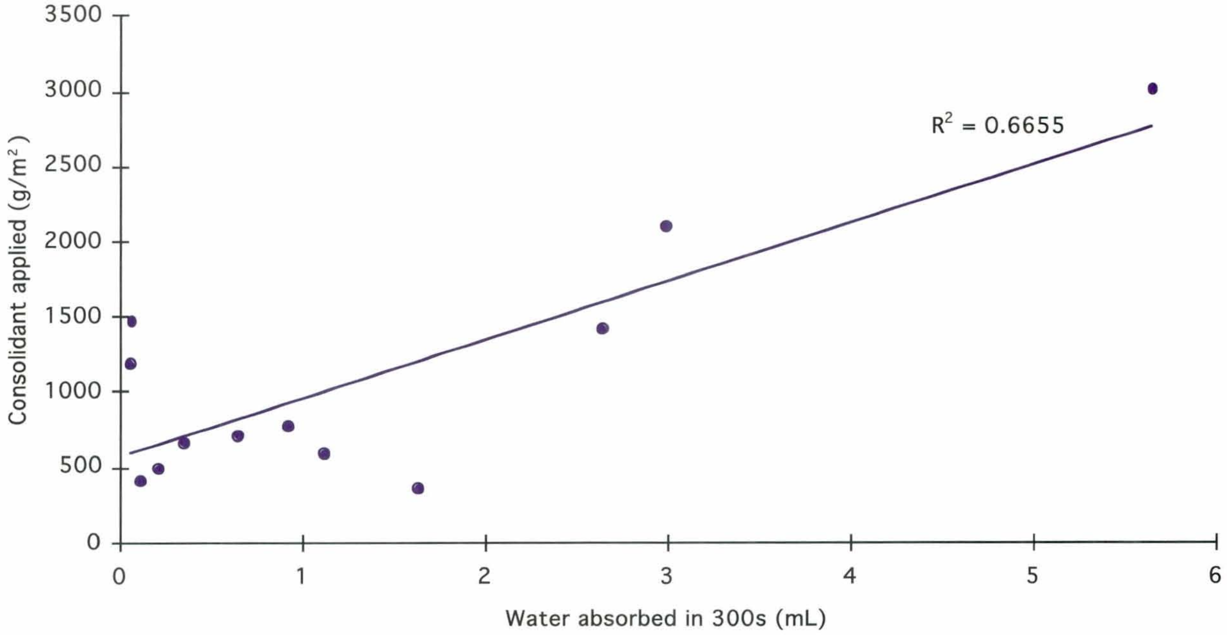

Figure 78c Relationship between amount of Water Rep./Con. C taken up by a sandstone and the amount of water taken up by the stone in 300 seconds.

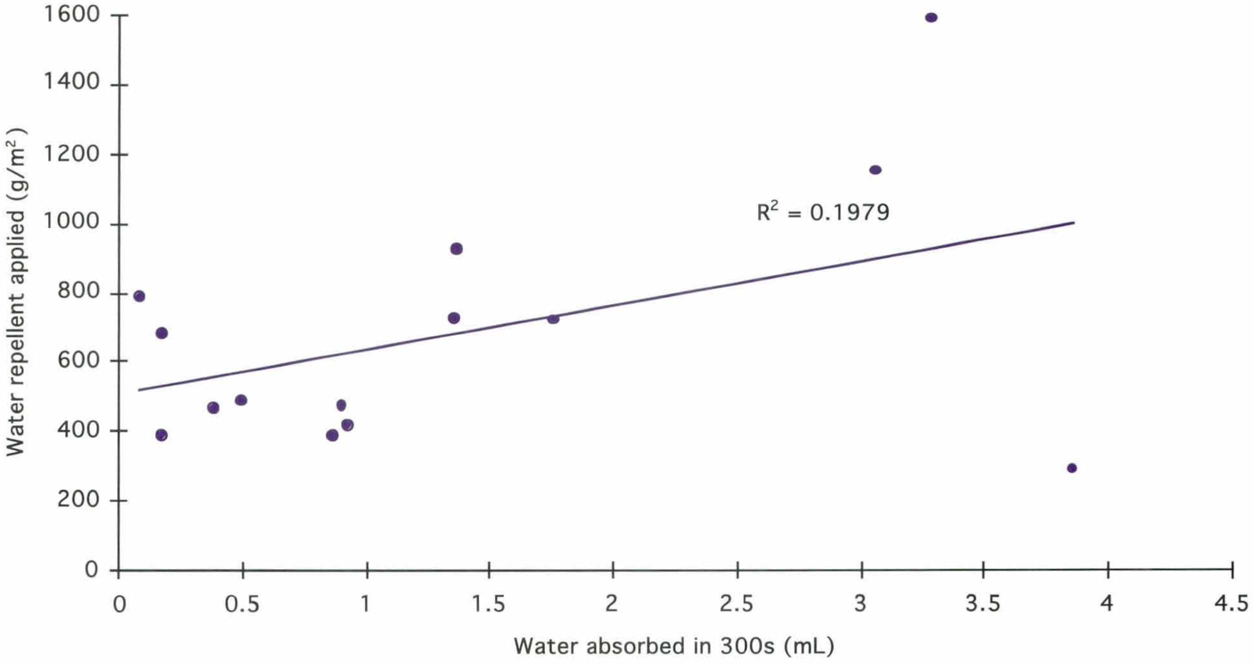

Figure 78d Relationship between amount of Water Repellent D taken up by a sandstone and the amount of water taken up by the stone in 300 seconds.

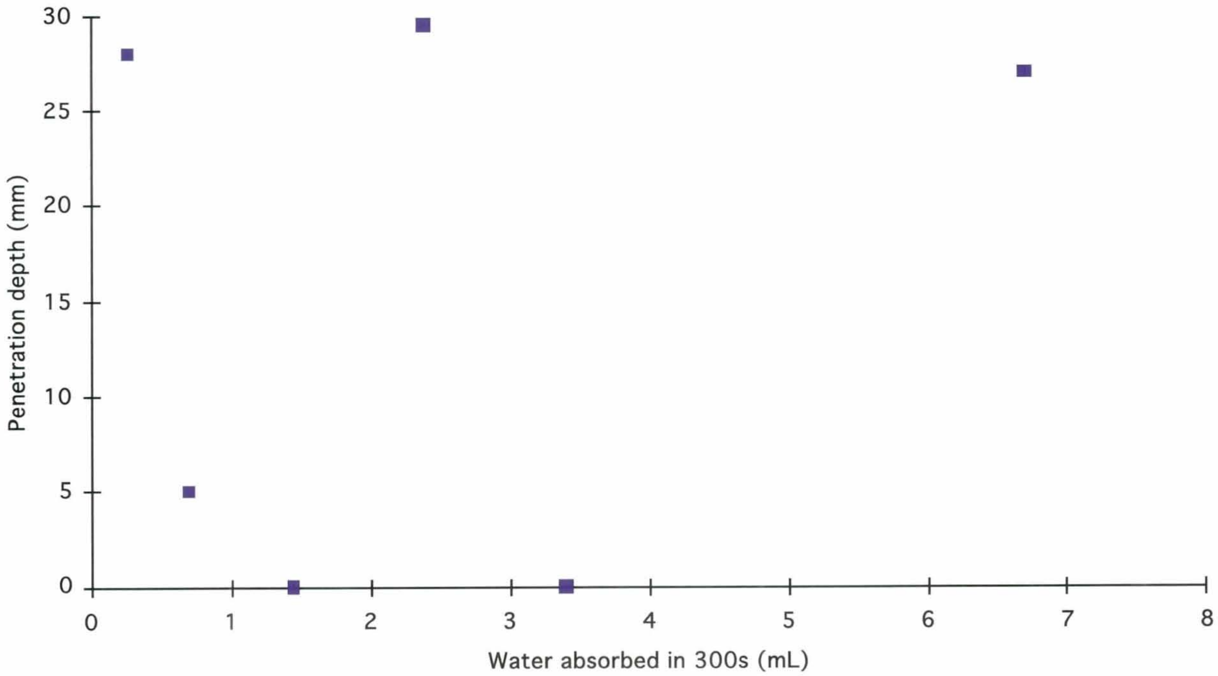

Figure 79a Relationship between penetration depth in Consolidant A and the amount of water taken up by the stone in 300 seconds.

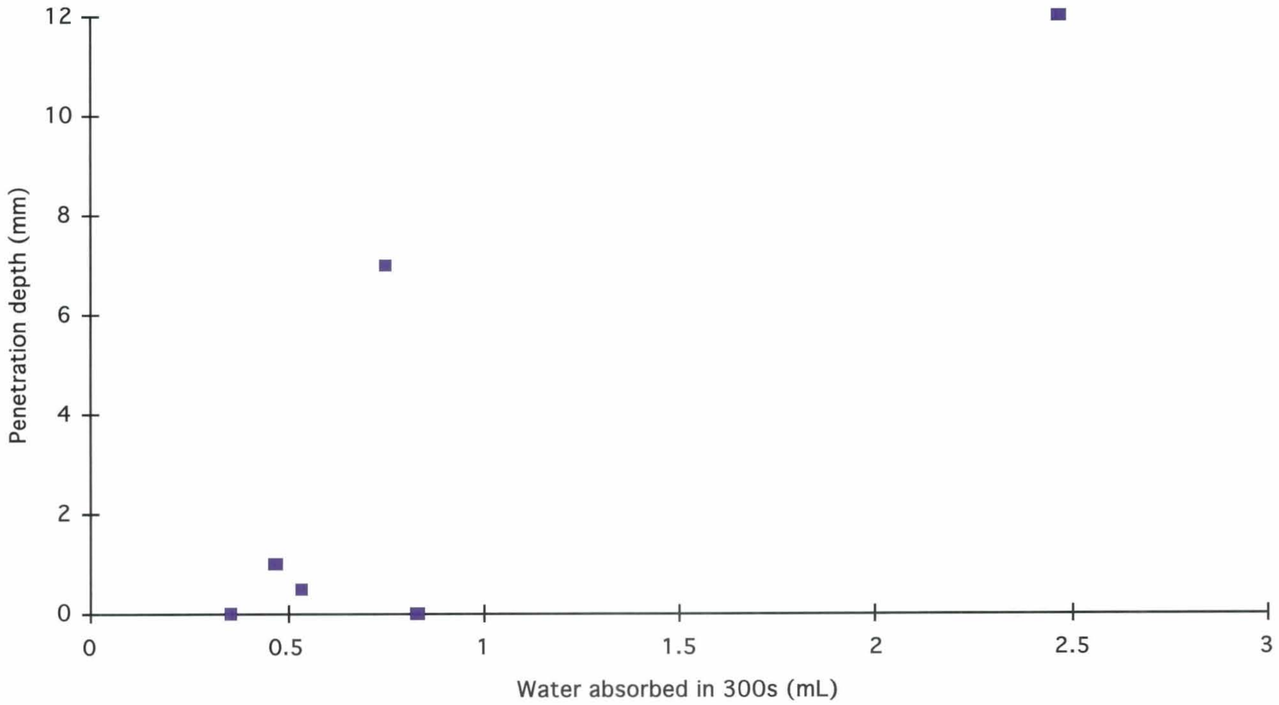

Figure 79b Relationship between penetration depth in Consolidant B and the amount of water taken up by the stone in 300 seconds.

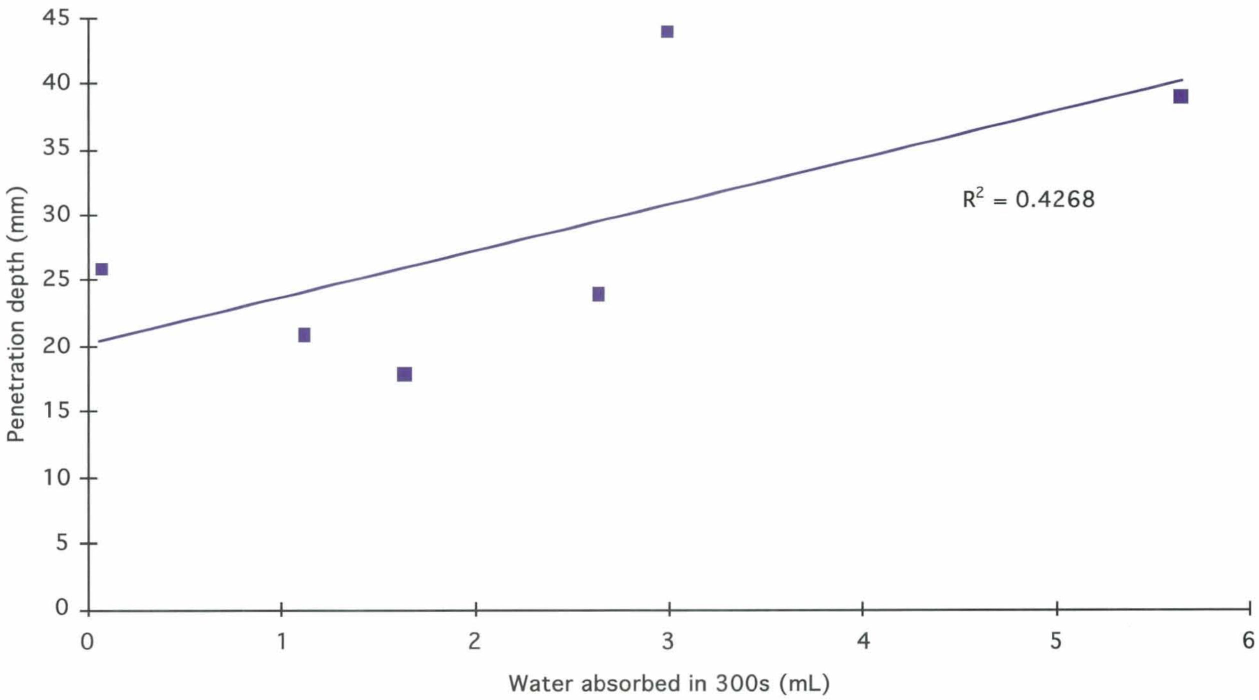

Figure 79c Relationship between penetration depth in Water Rep./Con. C and the amount of water taken up by the stone in 300 seconds.

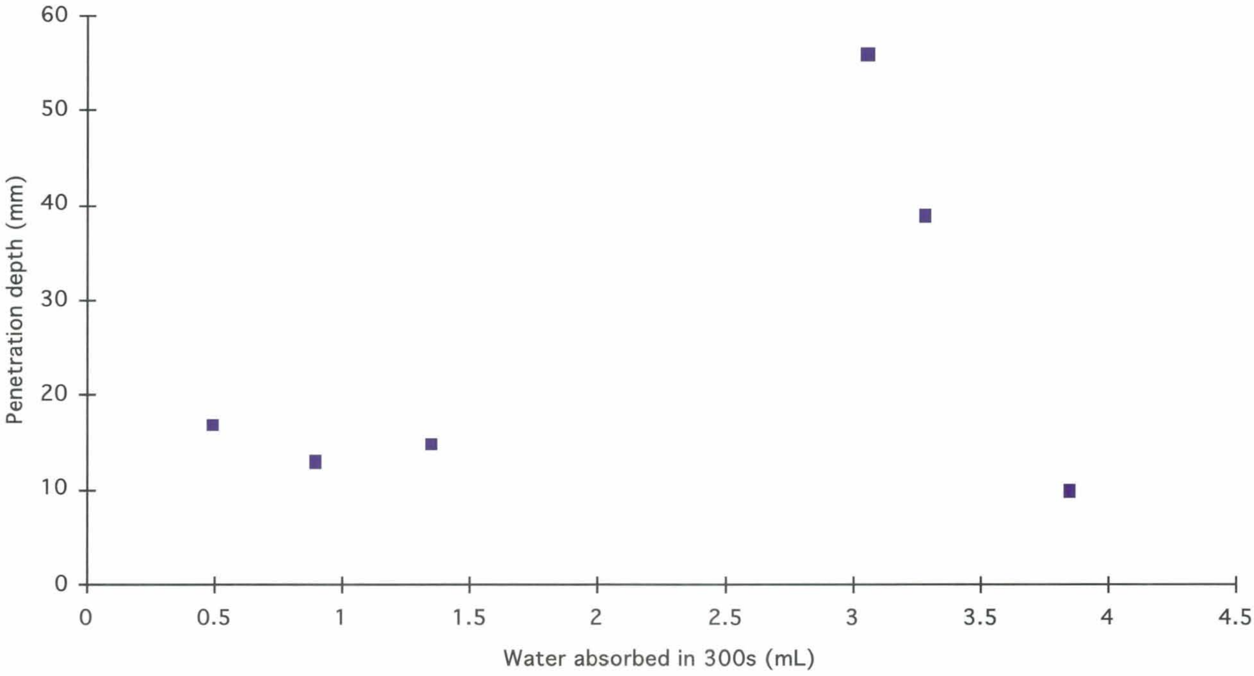

Figure 79d Relationship between penetration depth in Water Repellent D and the amount of water taken up by the stone in 300 seconds.

7.13 Field sites

Application of consolidants to the field sites in Elgin, Huntly, Arbroath, Dunkeld and Tantallon took place between about 1974 and 1986. Application was carried out by Historic Scotland (Elgin and Huntly) and by BRE (Arbroath, Dunkeld and Tantallon). The amount of data available regarding the treatments was variable, making interpretation of results difficult in some cases.

Cores were obtained from Arbroath, Dunkeld and Tantallon. The treatments used at these sites were mixtures of silanes, all of which had water repellent properties. Mercury porosimetry results indicated that none of the treatments had resulted in a significant loss of porosity. Examination of cores from treated samples showed that water repellency from treatments was still measurable on most cores 20 years after treatment although only the test panel at Arbroath still showed any surface water repellency.

The mean depth of penetration of water repellency was:

Arbroath Abbey: 35 mm

Dunkeld Cathedral: 24 mm

Tantallon Castle: 50 mm

This indicates that the methods of application used achieved good penetration, in all cases being beyond the expected depth of stone decay. While the amount of surface loss is difficult to assess due to the lack of measurable control areas, at Arbroath the continued water repellency on the surface suggests that granular losses from the surface have been largely prevented by the treatment. However, the possibility of long term sub-surface decay with associated spalling and potential catastrophic loss of large sheets of stone cannot be discounted.

Although no cores were taken at Elgin Cathedral, the evidence from examination of the surface appearance of the sandstone was that consolidant treatment had achieved a penetration of only 2-3 mm at most and that subsequently most of the treated sandstone surface had been lost. The consolidant used was a mixture of an acrylic and a silane. These results are consistent with those obtained from the test panels in Aberdeen where the depth of penetration of the acrylic (Consolidant A) was found to be only a few millimetres.

In contrast with results at Elgin, visual examination of the test panel at Huntly (also not cored) gave no indication of any serious problems. The relatively good preservation of this stone is likely to be due to a combination of the effects of the consolidant (Paraloid B-72) and the sheltering of the area from rainfall.

8 CONCLUSIONS

8.1 Laboratory compared to real building treatments

As far as possible the test panels constructed in Aberdeen and at Myers Hill, and the methods used for application of consolidants and water repellents, were designed to simulate the results which would be achievable on building facades. The sandstones selected were representative of those used in buildings and included both fresh and soiled examples. Samples treated in the laboratory are not representative of real buildings. Laboratory samples can be very effectively impregnated with consolidant to produce a strong consolidant effect. However, on real buildings it is not possible to achieve the volume of input that can be attained in the laboratory. Comparing results of treatment penetration and strength increases achieved in this, and other, field based studies with results of laboratory based experiments there was a wide difference in outcome - generally laboratory based applications produce better, more reproducible results. The differences between laboratory and field based tests include: applications method (e.g. soaking vs. brush), treatment loss through run-off, uncontrolled climatic effects (e.g. temperature, direct sunlight, rainfall, humidity), effects of mortar or joints, condition of surface, effects of soiling or biological growths, the inability to ensure complete dryness of the substrate and insulating effects due to surrounding (or lack of surrounding) masonry.

Laboratory based tests for depth of penetration may be useful indicators for sandstones where the volume of sample and its situation are a good simulation of the building facade. However, small samples cannot provide an accurate picture of treatment effects. Laboratory based tests on bulk mortar samples are unlikely to provide an accurate picture of the behaviour of treatments in mortar on building facades. The characteristics of bulk mortar have been found to be significantly different to those of mortar in joints due to differences in compaction and curing and the likely presence of cracks at joints in building facades, especially in cement mortars.

In order to make reliable predictions of consolidant or water repellent behaviour on buildings it is necessary to simulate, as far as possible, the conditions which will be encountered on building facades.

8.2 Consolidation and water repellency

Consolidants and water repellents are not two distinct types of material. Most treatments are a mixture of the two characteristics. Some are predominantly water repellents with little consolidative effect, others are mainly consolidants but also have a water repellent effect. Water repellents are intended to prevent liquid water access to masonry through the treated face while still allowing moisture evaporation. Consolidants are intended to strengthen decayed stone by replacing lost mineral cement and bonding loosened grains more strongly.

It remains unclear whether water repellent treatments require to be present only on the immediate surface of the stone or whether deeper penetration would be more desirable. If liquid water is likely to be present inside stone (e.g. where water penetration may occur through wall tops or where there is no DPC or through defective pointing) then deep penetration of water repellents may be disadvantageous since this will force moisture evaporation to occur within the body of the stone. If evaporation takes place within a narrow zone and involves precipitation of salts this could, over time, weaken the stone at that depth, leading eventually to spalling. However, deeply penetrating water repellents (which are still thoroughly vapour permeable) may be preferred where liquid water is unlikely to get behind the treated zone, especially as mortar joints and cracks can track surface water several centimetres into surfaces. Water repellents are likely to be effective where the requirement is to stop water penetrating the stone surface. They will be ineffective and potentially damaging where moisture may enter the stone through paths other than via the treated surface.

If consolidants are to be effective they need to penetrate the stone deeply, at least to beyond the depth of decay. If the consolidant does not penetrate to sound stone then this will result in the creation of a hardened outer layer over a weaker, decayed layer, a circumstance that is likely to eventually lead to spalling of the surface at the limit of penetration of the consolidant. In these experiments the deepest penetrations were achieved by Water Rep./Con. C and Water Repellent D; the two consolidants (Consolidants A & B) achieved only relatively low penetration (especially Consolidant B).

8.3 Volume of treatments absorbed

The amount of consolidant or water repellent absorbed by stonework can be an indication of likely depth of penetration and may be estimated by measuring the weight or volume of material applied. However, errors may arise due to losses through run-off, differential penetration into stones and mortar or (for some treatment methodologies) due to losses during solvent washing phases of the treatment. Losses of consolidant during the solvent washing stage are likely to be significant where the depth of penetration of the treatment is low.

The amount of absorption of applied consolidants may vary by up to 20 times depending on the porosity and permeability of the sandstone substrate. The state of decay of the sandstone is also an important influence on treatment absorption since decayed, weathered sandstones often take up more treatment than similar fresh sandstones.

The rate of absorption of consolidants and water repellents is affected by the solvent used and the viscosity of the treatment. Increasing viscosity may increase absorption, especially on stones where the absorption rate is slow, by keeping the treatment in contact with the stone for longer through reduced run-off rates. However, the more viscous the treatment, the slower will be its penetration once it is in the stone.

8.4 Strength tests and friable surfaces

For the consolidants and water repellents tested, the results of strength tests on treated sandstones indicated relatively little effect, although Consolidant A appeared to produce some slight strength increases at up to 15 mm depth. This is likely to be due to a combination of factors:

- Coring and testing of samples requires stone that is at least still fairly "stable". Even though samples of soiled stone in the tests included friable surfaces (as judged by how easily the sliced soiled cores fell apart at 2-3 mm thickness compared to cutting fresh cores), the consolidants were not able to supersede the residual strength left by the remaining stone structure.
- To consolidate extremely friable or "sand-like" areas of stone could only be carried out "on site" in uncontrolled tests.
- The treatment can easily soak away to other deeper areas of stone, thus reducing the strength of the consolidation.
- Some strength effects may only occur in the very surface, such as Consolidant B where treatment penetration was, in many cases, <2 mm.

The results of strength tests indicate therefore that stone has to be extremely friable if consolidants are to produce any effective increase in strength.

8.5 Changes in porosity due to treatments

None of the treatments tested were found to block porosity in the sandstones. However, some treatments (i.e. Consolidant A and Consolidant B) did reduce porosity by about 1.5-3%. Measurements of changes in water vapour permeability showed that treatments could cause reduction in permeability of up to 30%, but effects varied depending on the sandstone type and the treatment. No increased vulnerability to freeze-thaw damage was found with any of the treatments.

8.6 Changes in stone dimension due to treatments

Consolidants and water repellents may cause stone masonry to expand or contract. If this occurred over a large area it could result in cracking and delamination. Laboratory application of consolidants and water repellents to sandstones produced both expansions and contractions, some of which were larger than those caused by water soaking alone. The size of observed dimension changes were difficult to extrapolate to real buildings as there is little information available on the expansion and contraction which occurs normally on buildings surfaces due to water and temperature changes.

8.7 Colour changes caused by treatments

All the consolidants and water repellents tested caused colour changes, some more than others. The degree of colour change may reduce over time and some treatments appear to reduce the soiling rate of the stone. However, although the degree of colour change may vary, the appearance of the stone surface is likely to be permanently altered while the treatment remains present. Treatments mainly resulted in darkening of the surface, but some reddening and yellowing were also noted with most treatments. Light coloured sandstones may be especially vulnerable since colour changes can be most visible on light coloured stone. Colour changes can initially enhance small colour differences making small variations in the stone much more prominent. One treatment (Consolidant B) caused particularly obvious darker and lighter banding on Locharbriggs sandstone due to differences in the composition of bedding layers in the stone.

Washing-down with appropriate solvents after application may be necessary to minimise colour changes caused by excessive treatment retention at the surface.

The colour changes tend to make the stone appear slightly wet. However, for water repellent treatments, since water penetration is reduced, the degree of colour change of the stone during rainfall is reduced.

Water repellents appear to reduce the rate of soiling of the stone, presumably since they reduce the ability of soiling particles to adhere to the surface.

Although consolidants and water repellents were found to cause darkening of the stone, when solvent based treatments are applied to soiled stone there may be some soiling removal due to the washing and brushing during application, leaving the stone with a lighter appearance than in its previously soiled state. Another side effect of soiling removal is that, for heavily soiled sandstones, the soiling which is removed may be more water repellent than the treatment that is applied. Paradoxically this can mean that the water absorption of a treated, soiled surface may be greater after water repellent treatment than it was before.

8.8 Depth of penetration of treatments and depth tests

In sandstones, the depth of penetration of the treatments tested varied from close to 0 mm up to about 60 mm. Ranges of penetration achieved (from a range of tests) were:

Consolidant A:	**0-50 mm**
Consolidant B:	0-16 mm
Water Rep./Con. C:	0-44 mm
Water Repellent D:	0-56 mm

Penetrations close to zero were found in sandstones of low porosity and permeability (i.e. Leoch sandstone, porosity ~7%). High penetration depths were achieved on highly porous and permeable sandstones (i.e. Locharbriggs sandstone, porosity ~22%).

In mortars, penetration depth was found to vary depending on the mortar composition. Penetration was generally greatest in the less durable mortars. Effects varied with different treatments. Results indicated penetration depths of:

Lime mortar:	up to 40-80 mm
1:3:12 mortar:	up to 30-40 mm
1:1:6 mortar:	up to 25-30 mm

Examination of penetration into and adjacent to joints indicated that treatments often penetrated more deeply into the mortar and along cracks in joints than they did in sandstone. It is possible that in such situations water repellents could reverse the normal pattern of moisture loss in a wall, causing more moisture evaporation through the stone rather than through the mortar.

8.9 Comparison of different depth of penetration tests

There is no single test that effectively determines the depth of penetration of all treatments. However, conducting a limited range of tests is effective in building up a picture of the location and distribution of treatments within stone. Although it is possible to predict, within a margin of error, the likely penetration of treatments (where pre-existing data is available for calibration) the true penetration depth cannot be predicted with accuracy unless core samples are taken for analysis. It should also be remembered that depth of penetration is likely to vary between stones with different characteristics and that the effects of mortar type and joint condition can have a significant effect on penetration depth on a masonry surface. Treatments that retain a degree of water repellency are easiest to test for, as water-based tests for hydrophobicity can give a fast, effective measure of the depth of penetration. However, it has been found that for some treatments (e.g. Consolidant A) the degree of hydrophobicity of treated stone can vary over time as the consolidant matures. If water repellency changes over time, this may give a misleading indication of depth of penetration.

Although a wide range of tests can be used to determine depth of penetration it is often the case that each method will provide different results. This occurs because the physical characteristics that the tests measure may change between different treatments, and then change again at different depths of penetration with the same treatment. For example, while water repellency results may indicate a relatively deep penetration, strength changes may only occur at the surface. This could be because only a trace amount of treatment is required to provide water repellency.

Useful test methods for depth of penetration include:

- water droplet absorption time (for water repellent treatments only)
- visual observation of colour changes on wetting and drying (mainly water repellent treatments)
- water vapour permeability
- strength tests

With the techniques used here, attempts at predicting depth of penetration can only provide a range of expected values. If depth of penetration is required to be known accurately then there is no substitute for coring and measurement. Nevertheless, techniques which can be used to provide a rough estimate of depth of penetration include measurement of:

- volume of treatment applied
- water absorption rate
- porosity
- permeability

Prediction of depth of penetration can, however, only be made if there is pre-existing data linking measured depths of penetration to the above techniques so that a predictive calibration can be constructed. The depth of penetration is likely to vary if treatment concentration or solvent types are varied.

8.10 Volatile organic vapours and health hazards

Most consolidants and water repellents (and all the treatments tested here) are solvent based. Solvents are therefore lost to the atmosphere for some time after treatment. In some cases, components of the treatment and chemicals released during curing may also evaporate. These are given off as volatile organic compounds (VOCs). Depending on the depth of penetration and the type of treatment or solvent, emission of VOCs may occur for several weeks following treatment. In the initial stages these may be a fire hazard and most are hazardous to health, requiring face masks with appropriate filters to be used in the vicinity. The hazard from unpolymerised compounds in some consolidants (e.g. silanes) is unlikely to last for more than a few days as polymerisation is normally relatively rapid (although polymerisation may be inhibited in calcareous substrates). However, in confined spaces the concentration of solvents may continue to be hazardous to health for several weeks.

8.11 Chemical cleaning of treated surfaces

When water repellent treated sandstones were chemically cleaned it was found that the treatments substantially reduced the penetration and quantity of residues from chemical cleaning. In untreated sandstones, residues can be found at over 20 mm depth. In water repellent treated stones residues were mainly confined to the outer 2 mm. The amount of residual chemicals in treated stones was about 20-60% of the levels in untreated stones. While on the examples cleaned in the laboratory, water repellent treatment did not appear to interfere with soiling removal, some reduction or patchiness in soiling removal cannot be ruled out on larger masonry facades. These results appear to indicate that chemical cleaning carried out on water repellent treated sandstone should be less damaging than cleaning carried out on untreated sandstone. However, these data were taken from sandstone samples within a few weeks of cleaning. The effects of water repellents and consolidants with respect to the later redistribution of soluble salts in the sandstone is unknown.

8.12 Long term and exposure effects

Examination of the long term effects of consolidants and water repellents on field sites where treatment was carried out up to 20 years previously indicates that results can be very variable. Only five examples were studied and conclusive results cannot be obtained from so small a sample. However, in general, better results were obtained using silane based compounds than with acrylic. This difference is apparently due to the greater penetration depth of the silane materials. Acrylic compounds may, however, perform better where the treated surface is protected from wetting. Where a consolidant treatment cannot penetrate to sound stone the treated surface is likely to be lost. Water repellency can, in some circumstances, be retained on a treated surface for over 20 years. Even where the original surface is lost, water repellency is still retained inside the stone.

8.13 Recommended long term test methodologies

It has become apparent, in attempting to assess the long term effects of consolidants on field sites, that, if long term monitoring of test panels is planned in the future, a rigorous methodology for recording data is necessary. In particular, it is necessary to record the condition of the stone prior to treatment. Photographs of the test area are essential. Complete notes should be taken of the treatments applied, the methodology used and the amount of consolidant applied. Photographs of the actual treatment process would also be useful. If long term monitoring of changes to the stone are planned then stones should be treated only on one half of each block. This allows assessment of weathering effects, surface loss rates, colour changes, efflorescence, etc., on treated and untreated examples of the same stone type. Use of separate stone blocks as controls is inadequate since stones can vary in their composition and behaviour and comparison of decay rates is very difficult to make between different blocks. The test panel area should be photographed immediately after consolidant application and following curing of the treatment. Methods of testing that may also be usefully performed on test stones include:

- obtaining cores samples before and after treatment

  This allows determination of the mineral composition of the stone, measurement of its porosity and, on the treated core, measurement of the depth of penetration of the treatment.

- coring several years after treatment

  This allows long term monitoring of any changes in the structure of the treated stone (e.g. evidence of incipient decay) and changes in the water repellency or depth of penetration of the consolidant.

- colour measurement

  This allows assessment of colour changes following treatment and in the longer term.

- water absorption

  This can provide an indication of likely depth of penetration. Changes following treatment could indicate changes in the water repellency of treatments.

- depth profiling of soluble salts

  This allows determination of the salt loading of stone before treatment and could indicate changes in salt concentration due to changes in moisture movement in the years following treatment which could provide an early indication of accelerated decay.

9 SUMMARY

9.1 Criteria for successful treatment

In general, if a consolidant or water repellent treatment is to perform adequately there are certain criteria which must be met:

- The treatment should be compatible with the stone type.
- The treatment should have good adhesion.
- The treatment should penetrate the stone to at least 25 mm or to the depth of stone deterioration. (There is some disagreement in the literature as to whether water repellents in particular should be confined to the immediate surface or whether they should penetrate the stone more deeply).
- The treatment should have low viscosity, moderate surface tension, low average molecular weight and low reactivity within the first few hours following application. These factors should increase the penetration of the treatment into the stone although materials with too low a molecular weight may be drawn back towards the surface on evaporation of the solvent.
- The treatment should be capable of withstanding the full range of temperature variations likely to be encountered on a building facade.
- The treatment should not block the porosity of the stone or significantly reduce the rate of moisture transport through the stone.
- The treatment should not alter the porosity such as to make the stone vulnerable to freeze-thaw damage.
- The treatment should, when applied to deteriorated stone, alter it so as to match as closely as possible the physical properties of sound stone.
- The treatment should not cause colour or reflectance changes to the stone surface and should not discolour over time.
- The treatment should not be vulnerable to decay by salts, acids in rain water, atmospheric gases and pollutants or biological organisms.
- The treatment should weather at a similar rate to the sound stone.
- The treatment should have a low solvent content (for health and ecological reasons).

9.2 Consolidant and water repellent types

Water repellents are intended to prevent or reduce water penetration into stonework and so reduce the rate of decay. Consolidants are intended to strengthen weakened stone and slow the rate of surface loss by binding loosened stone through bridging of gaps between grains. Many treatments have a mixture of consolidant and water repellent characteristics. Some are predominantly water repellents with little consolidative effect, others are mainly consolidants but also have a water repellent effect. The treatments tested and used on stone are normally of a single material type. However, mixtures of treatments are also occasionally used.

Compound	Effects
Silane-based materials	These include a wide variety of organosilicon compounds that polymerise to form networks of silica gel. As the gel dehydrates it forms deposits of silica in the substrate. Some types (e.g. tetraalkoxysilanes) have no water repellent properties, others (e.g. alkyl trialkoxysilanes) have a degree of water repellency which can be controlled by altering the properties of starting material. Polysiloxanes are partially polymerised silanes. They are less volatile than silanes and are soluble in organic solvents. Silane-based materials are generally able to penetrate relatively deeply into a porous substrate although results can be variable. Significant strength improvements have been reported using silanes. The polymer is very stable and will not break down in UV light or when exposed to acid rain. However, it may break down in the presence of silane vapour during re-application of consolidant if the previous application has not fully cured
Acrylic consolidants	Acrylic resins that have been used on stone include methylacrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate. They can achieve substantial increases in the strength of the substrate. When it is free from impurities, polymethyl methacrylate (PMMA) is stable to degradation by heating, oxygenation and ultra-violet radiation and will not yellow with age. Other acrylics are less stable.
Vinyl consolidants	Vinyl consolidants include polyvinylchloride (PVC) and polyvinylacetate (PVA). These have generally been unsuccessful as stone consolidants since they tend to give the surface a glossy appearance and it is difficult to achieve good penetration.
Epoxies	Epoxy resins are formed by cross-linking of low molecular weight epoxy polymers. They can achieve substantial increases in the strength of a substrate. However, epoxy resins have generally been found to be impractical for use in the consolidation of sandstone due to their low penetration.
Polyurethane	Polyurethanes are introduced into stone in solvents and deposited as the solvent evaporates. Polyurethanes can achieve substantial increases in stone strength but are vulnerable to decay caused by exposure to heat or light, they may therefore include stabilisers.
Polyesters	Polyesters have poor resistance to UV radiation, acids and alkalis. Their long term performance is poor and they have not been found to be useful in stone conservation.
Perfluoropolyethers	Perfluoropolyethers are generally used as water repellents as they have little or no cohesive effect. Perfluoropolyethers are very stable to UV and are theoretically removable from stone through their solubility in fluorinated solvents. These products remain mobile within a stone and their performance therefore gradually declines over time. Degree of mobility is affected by the polarity and size of the functional groups and the porosity of the stone, the decline in protective efficacy being slower in less porous stone. These products therefore generally work best in stone types of lower porosity.
Fluosilicates	Fluosilicates of magnesium, zinc and aluminium have been tested as stone consolidants. However, acids are produced in their formation which will attack calcareous stones resulting in a hardened surface layer through deposition of calcium fluorides. Fluosilicate consolidation has been suspected of being responsible for exfoliation and accelerated deterioration of some treated sandstones.
Barium-hydroxide (limestone treatment)	Treatments involving barium hydroxide have been used for the consolidation of decayed limestone. Treatment with barium hydroxide, in addition to the formation of barium carbonate, also results in the transformation of calcium sulphate into the relatively insoluble barium sulphate. Treatments in the past have followed the barium compound with a second acid solution to form an insoluble precipitate with the barium. Silicic, fluosilicic, carbonic, sulphuric, chromic and phosphoric acids have been used. Disadvantages of these treatments include colour or textural changes and the short term nature of any consolidation effects.
Limewater (limestone treatment)	Lime has been used as a consolidant for limestones. Lime is converted into calcium carbonate by carbonation in contact with the atmosphere. Results have varied and while some authors report good outcomes others have found results to be poor.

Table 38 Notes on composition and effects of consolidant and water repellent treatments on sandstone (unless otherwise stated).

9.3 Potential problems

9.3.1 Depth of penetration

- Different measurement techniques may give very different values for depth of penetration. For instance, the depth of hydrophobic effects may be greater than the depth at which significant strengthening is measurable but less than the depth at which the treatment is detectable.
- If it is assumed that penetration depth should be at least 25 mm, only a few silane and polyurethane treatments would be considered effective. Acrylics, vinyls, epoxies, polyurethanes, fluosilicates and perfluoropolyethers often have poor penetration (however, water repellent treatments may not require deep penetration).
- Where penetration depth is low, problems may arise with surface spalling, salt crystallisation or frost damage below the treated layer.
- Many consolidants are dissolved in solvents to give them a low enough viscosity to penetrate the substrate. The polymers are then deposited as the solvent evaporates. If evaporation is too rapid, the consolidants may be drawn back and deposited at the surface.
- Monomeric silanes are volatile and may evaporate from a surface before polymerisation takes place.
- If vaporised monomers are condensed on other surfaces, polymerisation may take place outwith the area intended to be consolidated.
- The polymerisation reaction of silanes requires the presence of water. If there is a lack of water then hydration will not proceed to completion and much of the consolidant may be lost in evaporation.
- While silanes require the presence of water to achieve polymerisation, the presence of moisture in a substrate may inhibit polymerisation and penetration of other treatment types (e.g. acrylics).

9.3.2 Polymer formation

- Where a stone is heavily contaminated with salts, this can interfere with polymerisation and adhesion of silane-base materials.
- The presence of calcite in a stone retards polymerisation of silanes.
- Polymerisation of silanes is faster at higher relative humidity, however, faster polymerisation may result in the accumulation of stresses in the polymer which may later result in cracking.
- Where a treatment undergoes a reduction in volume on setting this may result in stresses being set up in the stone if the material adheres to the mineral grains before shrinkage is complete.
- The final form of the polymer derived from silane-based materials has been found to be strongly dependent on the type of solvent used, the presence of any catalysts and even the mixing method.
- Re-application of silane-based treatments can cause swelling of the previous treatment if it has not had sufficient time to become fully cured.

9.3.3 Polymer stability

- Silane-based polymers are generally very stable. However, some other treatment types may alter as they age, through the action of light, heat, moisture, physical or chemical attack or the action of biological organisms.
- Many organic polymers are vulnerable to degradation when exposed to heat, ultra-violet light or acids.
- Organic polymers may also be broken down by the action of microorganisms, which may use the organic polymer as a food source.

9.3.4 Colour changes

- Changes to the appearance and colour of substrates may occur with any consolidant or water repellent treatment including silanes, acrylics, vinyls, epoxies, polyurethanes and fluosilicates. Degree of colour change varies depending on the substrate, treatment and application method and under some circumstances some treatments do not cause colour changes.

- Colour differences may be apparent on the substrate in both wet and dry conditions. Water repellents especially can change the normal appearance of stone when exposed to rainfall.
- Vinyl polymers turn white and opaque when wetted but revert to a clear state on drying.
- Glossiness may occur due to deposition of polymers on a stone surface.
- Colour changes may occur due to changes in the characteristics of a polymer over time. Polymer materials vary in their vulnerability to degradation but some, including some acrylics, epoxies and polyesters, degrade rapidly when exposed to ultra-violet radiation.
- Polymers which are relatively soft (e.g. some vinyl polymers) may attract soiling.

9.3.5 Physical changes

- Treatments can affect both moisture absorption and evaporation rates in unpredictable ways.
- While water repellents can prevent or reduce ingress of liquid water through the stone surface they cannot prevent ingress of water in the vapour phase, through cracks at mortar joints, by rising damp or by transfer from surrounding stonework. Therefore, although a water repellent could reduce the amount of moisture penetrating a stone, it cannot guarantee to exclude all moisture and, given that many applied materials reduce the rate of evaporation of moisture from a stone, it is not clear that a water repellent will reduce the duration of dampness in a stone.
- It is important that treatment does not cause a substantial reduction in substrate porosity as the mortar and treated stone must be able to lose moisture by evaporation to prevent trapping of moisture behind the treated zone.
- Porosity change may alter the vulnerability of stones to damage by salt crystallisation or freeze-thaw.
- The degree of expansion and contraction of the treated substrate on heating and cooling should be as close as possible to that of the surrounding sound substrate to avoid detachment of the treated area.
- Some consolidants and water repellents-consolidants have been found to be capable of achieving substantial increases in strength in treated stones. It is not necessarily the case that stronger is better since, in general, the only requirement of the consolidant is to reduce the rate of decay of the stone surface by re-cementing loosened grains. The surface is not generally required to bear any loads and does not therefore require to be particularly strong. Over-strengthening the surface could lead to problems including differences in thermal expansion, blockage of porosity or increased brittleness which could result in flaking and spalling of the treated surface.

9.3.6 Increased vulnerability to decay

- If a consolidant increases the proportion of fine pores in a substrate, this can result in increased susceptibility to frost damage.
- A number of treatments including silanes, acrylics and polyurethanes have been found to increase the vulnerability of sandstone to decay linked to salt crystallisation. However, in a number of cases a decrease in vulnerability was noted. At present it is not possible to predict the effects of treatments with respect to vulnerability to salt decay.
- Fluosilicate treatments may result in formation of soluble salts in a substrate.
- Where soluble salts are present in an untreated stone, capillary forces generated by evaporation of water at the surface will cause these salts to be deposited on or near the surface. In water repellent treated stone, water cannot move out to the surface and must evaporate inside the stone, beyond the limit of penetration of the water repellent. This may result in the deposition and concentration of soluble salts within the stone. Damage to the stone through crystal growth pressure or volume changes may then result.
- Some silane treatments have been found to have the potential to increase the vulnerability of sandstone to decay processes caused by acid mists.

9.3.7 Emissions of solvents

- Emission of volatile organic compounds (VOCs) may occur for several weeks following treatment. In the initial stages these may be a fire hazard and most are hazardous to health requiring face masks with appropriate filters to be used in the vicinity. The hazard from unpolymerised compounds in some consolidants (e.g. silanes) is unlikely to last for more than a few days as polymerisation is normally relatively rapid. However, in confined spaces the concentration of solvents may continue to be hazardous to health for several weeks.

9.4 Method of application and uptake of treatment

The method of application can be very important with respect to the depth of penetration of consolidant or water repellent treatments. Application methods (both field and laboratory based) include: brushing, spraying, dripwise application, capillary absorption, vacuum impregnation, pressure impregnation and total immersion. Depths of penetration achievable in laboratory settings may not necessarily be achievable in the field. Unless the laboratory method reproduces, as far as possible, conditions likely to be found in the field, results are unlikely to reflect those encountered on a building facade.

The amount of treatment absorbed may vary widely depending on the porosity and permeability of the substrate. The state of decay of the stone is also an important influence on treatment absorption since decayed, weathered stones often take up more treatment than relatively intact stone. Rates of absorption of treatments are also affected by the solvent used and the viscosity of the treatment. Deep penetration of stone cannot be achieved if the preservative substance polymerises too rapidly. Some systems therefore add catalysts to the monomer-solvent mixture which cause rapid, but delayed, setting or gelation at some time after application.

The amount of consolidant or water repellent absorbed by stonework can be an indication of likely depth of penetration and may be estimated by measuring the weight or volume of material applied. Errors may arise due to losses through run-off, differential penetration into stones and mortar or (for some treatment methodologies) due to losses during solvent washing phases of the treatment. Losses of consolidant during the solvent washing stage are likely to be significant where the depth of penetration of the treatment is low.

For the sandstone tested here, the depth of penetration of the treatments varied from close to zero up to about 60 mm depending on treatment type and stone characteristics. Penetrations close to zero were found in sandstones of low porosity and permeability. High penetration depths were achieved on highly porous and permeable sandstones. In mortars, penetration depth varied from a few millimetres up to 80 mm depending on the mortar composition. Penetration was often greater along joints than in either the mortar or sandstone.

9.5 Assessment of treatment effectiveness

There are a number of factors that may be involved in assessing the performance of any consolidant or water repellent treatment. These can include:

- depth of penetration of treatment,
- changes in strength,
- changes to porosity,
- changes to permeability,
- changes in water retention and absorption characteristics,
- changes in colour,
- changes in thermal expansion and contraction.

If depth of penetration is required to be known accurately then there is no substitute for coring and measurement. However, a rough indication of depth of penetration may be gained from measurements of the volume of treatment applied, water absorption rate, sandstone porosity or permeability measurements, provided that pre-existing data on measured penetration depths are available to provide a comparison. There is no single test that effectively determines the depth of penetration of all treatments. For water repellent treatments, tests for hydrophobicity on core samples can give a fast, effective measure of the depth of penetration. Non-hydrophobic treatments may require other test methods such as strength tests. Different test methods may yield different penetration depths on the same sample since measured characteristics may vary in their effectiveness. For example, while water repellency results may indicate a relatively deep penetration, strength changes may occur only at the near surface. Although it is possible to predict, within a margin of error, the likely penetration of treatments, the true penetration depth cannot be predicted with accuracy unless core samples are taken for analysis. Depth of penetration varies between stones with different characteristics and the effects of mortar type and joint condition can have a significant effect on penetration depth on a masonry surface.

Useful test methods for measuring depth of penetration include:

- water droplet absorption time (water repellent treatments only)
- visual observation of colour changes on wetting and drying (mainly water repellent treatments)
- water vapour permeability
- strength tests

For the consolidants treatments tested here, the results of strength tests on treated sandstones indicated only relatively slight increases in strength. However, these samples included mainly fresh and soiled sandstones, rather than highly decayed stone. Other investigators have found substantial increases in strength on application of silanes, acrylics, epoxies and polyurethane consolidants. This suggests that stone has to be extremely friable if consolidants are to produce any effective increase in strength.

None of the treatments tested here were found to significantly block porosity in the sandstones. However, some treatments did reduce porosity by about 1.5-3%. Other investigators have found some reduction in porosity with silane-based treatments. Measurements of changes in water vapour permeability showed that some treatments tested here could cause reductions in permeability of up to 30%. Other investigators have found evidence of reduction in water absorption for silane, acrylic, epoxy and polyurethane treatments.

All the consolidants and water repellents tested here caused colour changes, some more than others. The degree of colour change may reduce over time and some treatments appear to reduce the soiling rate of the stone. However, although the degree of colour change may vary, the appearance of the stone surface is likely to be permanently altered while the treatment remains present. Treatments mainly resulted in darkening of the surface although slight colour changes may also occur. Light coloured sandstones may be especially vulnerable since colour changes can be most visible on light coloured stone. Colour changes may also differentially enhance small colour differences in the original stone colour. Washing-down with appropriate solvents after application may be necessary to minimise colour changes caused by excessive treatment retention at the surface.

Laboratory results from sandstones treated here indicated that effects on thermal expansion and contraction of treated stone were small but measurable. The implications of these results are difficult to extrapolate in terms of behaviour on a building facade, however, substantial differences in thermal behaviour relative to the underlying stone can result in detachment of a treated surface.

9.6 Laboratory results compared to real building treatments

While there are many reports on performance of water repellents and consolidants in laboratory based situations, practitioners should be aware that results from stone samples treated in the laboratory are not necessarily representative of those that would be obtained on real buildings. In the laboratory, samples can be very effectively impregnated. However, on real buildings it is seldom possible to achieve the same level of control. Laboratory based applications therefore produce better, more reproducible results than can generally be expected in the field. Despite these difficulties, laboratory based tests can provide a useful indication of the potential performance of a treatment where the volume of sample and its situation are a good simulation of the building facade.

Laboratory based tests on bulk mortar samples are unlikely to provide an accurate picture of the behaviour of treatments on mortar on building facades. The characteristics of bulk mortar have been found to be significantly different to those of mortar in joints due to differences in compaction and curing and the likely presence of cracks at joints in building facades, especially in cement mortars.

9.7 Long term effects

The effective life span of treatments is relatively little studied beyond one or two years. It is therefore not possible to draw any general conclusions from the limited data available. However, some characteristics of particular polymers make them unlikely to be suitable for long term use on buildings. These include polymers that are unstable under ambient conditions of light, temperature or moisture.

Examination of the long term effects of consolidants and water repellents on field sites where treatment was carried out up to 20 years previously indicates that results can be very variable. Water repellency can, in some circumstances, be retained on a relatively stable, treated surface for over 20 years while the surrounding areas may be very decayed and apparently in a bad state of recession. The treatment may still be detectable (in terms of its water repellency) to a considerable depth. Even where the original surface is lost, water repellency may still be retained inside the stone. In general, better results appear to be obtained using silane-based compounds than with acrylic compounds. This difference is apparently due to the greater penetration depth of the silane materials. Acrylic compounds may, however, perform better where the treated surface is protected from wetting.

Opinion is divided on the use of water repellent materials since they alter the characteristics of the stone with respect to water absorption and evaporation. For both water repellents and consolidants there is no agreement as to what represents an appropriate treatment depth. Some investigators suggest that water repellents might be most appropriately applied only to the immediate surface, whereas others suggest that deep treatments are more appropriate. Water repellents are likely to be effective where the requirement is to stop water penetrating the stone surface. They will be ineffective and potentially damaging where moisture may enter the stone through paths other than via the treated surface.

For consolidant treatments, there is agreement that treatments confined to the outer surface are dangerous since they can result in spalling of the stone but there is no agreement on what would be an appropriate depth of treatment beyond the fact that it is obviously necessary to treat the stone deeply enough to consolidate the full thickness of the decayed zone. Some stone consolidants also have water repellent properties. Since it is dangerous to confine consolidation to the near surface this makes the use of a combined water repellent-consolidant problematic if it is considered best to confine water repellency characteristics to the outer surface.

The ideal polymer for use in stone consolidation would be one that can reverse the degradation of a stone, returning it as nearly as possible to its original condition. In order to achieve this the treated stone should mimic sound stone in as many characteristics as possible. Some characteristics are, however, more important than others. The most important include strength, porosity, permeability, thermal dilation and colour. Of all the polymers tested, silanes seem to hold out the most promise although they may not be suitable in every situation. The theoretical end product of polymerisation of the simplest silanes is silica, which is present as a cementing mineral in many sandstones, and may mimic the behaviour of a natural cement more closely than many other polymers.

APPENDIX
CHEMICAL DATA AND SAFETY INFORMATION

A.1 Chemical information

The tables in the following pages provide information derived from the published literature and from manufacturers' guidance on the composition and behaviour of consolidants and water repellents.

A.2 Health and safety

All consolidants and water repellents should be supplied with a manufacturer's safety data sheet which will provide information on the precautions to be taken during application. It is essential that those working with the materials and any other persons in the vicinity are suitably protected. Many consolidant and water repellent treatments contain solvent compounds which should be considered flammable. After treatment it may be difficult to determine exactly when the health and fire risks have reduced. In exposed locations the fumes probably diffuse away quickly. In enclosed areas the fumes may remain for several days. Manufacturers' instructions for some of the products recommend sealing treated surfaces with foil or plastic to contain the solvents and consolidants vapours for up to two weeks. When treated surfaces are sealed in this way the areas contained may be highly flammable and will still pose health risks.

Loss of unpolymerised compounds may be a safety concern since many consolidant or water repellent treatments contain silane monomers which are extremely hazardous to health, being damaging to both eyes and lungs. Since polymerisation is normally fairly rapid, this hazard is unlikely to persist for longer than, at most, a few days following treatment. However, there is no guidance from the manufacturers with respect to loss of unpolymerised compounds. As a result it should be assumed that there may be some long-term emissions of VOCs over several months.

Table A.1 *Data on consolidants and water repellents. Product and chemical information.*

Product	Function	Type	Chemical	Solvent/s	Catalyst
Wacker OH (Wacker-Chemie GmbH) Conservare OH Stone Strengthener Steinfestiger OH SS-301 (Colcoat Co.) Tegovakon V (Th. Goldschmidt SA) HAS 6 (Colcoat Co.)	Consolidant	Silane	Tetraethoxysilane	Acetone ketone toluene methanol white spirit ethanol	Dibutyltindilaurate
Brethane (Colebrand Pty. Ltd.) Z-6070 (Dow Corning) DF104 (General Electric) & others	Consolidant & water repellent	Silane	Methyltrimethoxysilane	methanol ethanol propanol 1,1,1-trichloroethane white spirit aromatics water	Yes
A1100 (Union Carbide) N2 (Petrarch Systems)	Consolidant & water repellent	Silane	Gamma-aminopropyl-trimethoxysilane or N-2-aminoethyl-3-aminopropyl-trimethoxysilane	*No data*	*No data*
(Petrarch Systems)	Consolidant	Silane	Gamma-glycidoxypropyl-trimethoxysilane	*No data*	*No data*
Z6030 (Dow Corning) 460 (Mased)	Consolidant	Silane	Gamma-methacryloxypropyl-trimethoxysilane or acrylic-silane emulsion	water	*No data*
Wacker H (Wacker Chemie GmbH) Conservare H SS-101 (Colcoat Co.) & others	Consolidant & water repellent	Silane	Methyltriethoxysilane	acetone ketone	Dibutyltindilaurate or trichloracetic acid
No data	Consolidant & water repellent	Silane	Methyltributoxysilane + dimethyldibutoxysilane	*No data*	Trichloracetic acid
Wacker 290 (Wacker Chemie GmbH) VP 1311 (Wacker Chemie GmbH) Wacker 290L (Wacker Chemie GmbH) Rhodorsil X-54802 (Rhone-Poulenc Italia SpA) Degussa WS 405	Consolidant & water repellent	Silane	Alkylalkoxysilane	water xylene white spirit	*No data*
RC70 (Rhone-Poulenc Italia SpA) RC80 (Rhone-Poulenc Italia SpA) RC90 (Rhone-Poulenc Italia SpA)	Consolidant & water repellent	Silane + siloxane	Partially polymerised alkoxysilane	white spirit	*No data*
Rhodorsil 224 (Rhone-Poulenc Italia SpA) Rhodorsil 4673 (Rhone-Poulenc Italia SpA) M.S. Siloxane (HEY'DI) Tegosivin HL-100 (Th. Goldschmidt SA or Tego Italiana Srl) Wacker 090 (Wacker Chemie GmbH) Dialsil C (Texa)	Consolidant & water repellent	Siloxane	Methylsiloxane	white spirit xylene trichloroethanol	*No data*
Neolith 76	Water repellent	Silicone	Silicone	Aromatic & aliphatic hydrocarbon	*No data*
No data	Water repellent	Siloxane	Hydrogenmethylsiloxane + barium hydroxide	*No data*	*No data*

Table A.2 Data on consolidants and water repellents. Physical and colour change data.

Product	Function	Type	Chemical	Solvent	Catalyst
Rhodorsil XR-893 (Rhone-Poulenc Italia SpA) Rhodorsil 10336 (Rhone-Poulenc Italia SpA) Rhodorsil 11309 (Rhone-Poulenc Italia SpA)	Consolidant & water repellent	Siloxane	Methylphenylsiloxane	aromatics	*No data*
No data	Consolidant & water repellent	Silane modified silica ester	*No data*	*No data*	*No data*
Baysilone (Bayer)	Water repellent	Silicone resin	*No data*	*No data*	*No data*
BS28 (Wacker Chemie GmbH) & others	Water repellent	Organosilicic	*No data*	xylene	*No data*
No data	Consolidant	Acrylic	Methylmethacrylate	toluene	Dibenzoyl peroxide
Dial PMA (Texa)	Consolidant	Acrylic	Methylacrylate	*No data*	*No data*
Paraloid B-72 (Rohm-Haas)	Consolidant & water repellent	Acrylic	Methylacrylate + ethylmethacrylate	toluene methylene trichloride xylene	*No data*
No data	Consolidant & water repellent	Acrylic	Butylmethacrylate	toluene	Dibenzoyl peroxide
Consolidant 55050 (ARD Raccanello) ARD (Vernici Racanell)	Water repellent	Acrylsiliconic resin	*No data*	*No data*	*No data*
Epo-tek 301A (Epoxy Technologies) Araldyt XB2697 (Ciba-Geigy) Araldite AY 103/HY 956 (Ciba-Geigy) & others	Consolidant & water repellent	Epoxy resin	Bisphenol A epoxy resin Dian-epichlorhydrine with organic amine hardener & other compositions	*No data*	Tetraamine
Desmodur N-3390 (Mobay) Phoba 10 (Hispanoquimica SA) Oxanpierre P/529/PIE (Metalfix) & others	Consolidant & water repellent	Polyurethane	Hexamethylene diisocyanate 30% isocyanate functionalised prepolymer and other compounds	1-methoxy-2 propylacetate	*No data*
No data	Consolidant & water repellent	Organosilicone-modified polyurethane	*No data*	*No data*	*No data*
FU 620 W FU 660 W FU 50	Water repellent	Polyfluorourethane	*No data*	water emulsion ethyl acetate	*No data*
No data	Consolidant & water repellent	Polyfluorourethane + perfluoropolyether copolymer	*No data*	water	*No data*
Akeogard PF (Syremont) Fomblin YR (Montefluos or Ausimont SpA) Fomblin YU (Montefluos or Ausimont SpA) Fomblin Y04 (Montefluos or Ausimont SpA) Fomblin MET (Montefluos or Ausimont SpA) & others	Water repellent	Perfluoropolyether	*No data*	1:1 Freon 11 & 12 Algofrene 113 trichlorofluoromethane trichlorotrifluoroethane dichlorodifluoromethane	*No data*
(Ausimont)	Water repellent	Perfluoropolyether	Perfluoropolyether with isobutyl ester functional groups	perfluorated chlorofluorated	*No data*

Product	Function	Type	Chemical	Solvent	Catalyst
(Ausimont & RPE-Carlo Erba Analyticals [ethylenediamide] & Janssen [hexamethylene-diamide]) Fomblin S12 (Ausimont SpA) Akeogard Ba (Syremont)	Water repellent	Perfluoropolyether	Perfluoropolyether with amide functional groups including isobutylamide of perfluoropolyetheric acid & neutral perfluoropolyether	perfluorated chlorofluorated trifluorotrichloroethane isopropanol	*No data*
Barra fluato (Ital-Barra)	Consolidant	Fluosilicate	Aluminium magnesium fluosilicate	*No data*	*No data*
No data	Consolidant	Fluoride	*No data*	*No data*	*No data*
No data	Consolidant	Polyester	Unsaturated dicarboxylic acid dissolved in styrene	*No data*	*No data*
Stratyl A 228 (Rhone-Progil)	Consolidant	Styrene-polyester resin	*No data*	*No data*	*No data*
No data	Consolidant	Inorganic	Various mixtures of Ca-hydroxide, Ca-carbonate & Portland cement	*No data*	*No data*
No data	Consolidant	*No data*	Hexafluoropropene-vinylidene fluoride elastomer	acetone water + butyl acetate	*No data*
Transkote (Sandtex Italiana)	Water repellent	*No data*	Aluminium strearate	organic	*No data*
Prot-edil	Water repellent	Amine	Emulsion of aliphatic amines	naphtha	*No data*

Mixed treatments :

Product	Function	Type	Chemical	Solvent	Catalyst
Wacker OH + Wacker 280 (Wacker-Chemie GmbH)	Consolidant & water repellent	Silanes	Tetraethoxysilane then alkylalkoxysilane	white spirit	Tin compound
Paraloid B-72 (Rohm-Haas) + Silicone Dri Film 104 (General Electric)	Consolidant	Acrylic + silane	Copolymer of methylacrylate + ethylmethacrylate then polymethylsiloxane	*No data*	*No data*
Paraloid B-72 + silane (Rohm-Haas)	Consolidant & water repellent	Acrylic + silane	Copolymer of methylacrylate + ethylmethacrylate then methyltrimethoxysilane	*No data*	*No data*
Paraloid B-72 (Rohm-Haas) + Z-6070 (Dow Corning)	Consolidant & water repellent	Acrylic + silane	Copolymer of methylacrylate + ethylmethacrylate dissolved in methyltrimethoxysilane	*No data*	*No data*
Paraloid B-72 (Rohm-Haas) + M.S. Siloxane (HEY'DI)	Consolidant & water repellent	Acrylic + siloxane	Copolymer of methylacrylate + ethylmethacrylate dissolved in methylpolysiloxane	*No data*	*No data*
Araldyt DY022 (Ciba-Geigy) + Dynasil A (Dynamit Nobel)	Consolidant	Epoxy + silane	Epoxy monomer + tetraethyl-orthosilicate	*No data*	*No data*

Product	Effects on strength	Penetration	UV stability	Colour	Abrasion resistance	Salt crystallisation	Frost damage
Wacker OH (Wacker-Chemie GmbH) Conservare OH Stone Strengthener Steinfestiger OH SS-301 (Colcoat Co.) Tegovakon V (Th. Goldschmidt SA) HAS 6 (Colcoat Co.)	Some sandstones show substantial increases in flexural & compressive strength, hardness & modulus of rupture. Tensile strength may be slightly increased.	Varies from "poor" up to 80 mm.	Stable	White deposits or darkening sometimes observed.	May be significantly improved.	Variable from no change to increased vulnerability.	*No data*
Brethane (Colebrand Pty. Ltd.) Z-6070 (Dow Corning) DF104 (General Electric) & others	Compressive & tensile strength, hardness & modulus of rupture may be substantially increased.	Up to 20 mm.	Stable	Sometimes darkening or glossiness observed.	*No data*	*No data*	*No data*
A1100 (Union Carbide) N2 (Petrarch Systems)	Modulus of rupture substantially increased.	*No data*	*No data*	Darkens stone.	*No data*	*No data*	*No data*
(Petrarch Systems)	Modulus of rupture substantially increased.	*No data*	*No data*	Darkens stone.	*No data*	*No data*	*No data*
Z6030 (Dow Corning) 460 (Mased)	Modulus of rupture slightly increased.	Up to 1 cm	*No data*	*No data*	*No data*	*No data*	*No data*
Wacker H (Wacker Chemie GmbH) Conservare H SS-101 (Colcoat Co.) & others	Compressive strength, hardness & modulus of rupture may be substantially increased.	Results vary, may be up to 25 mm.	Stable	White deposits sometimes observed.	*No data*	*No data*	*No data*
Methyltributoxysilane	*No data*	*No data*	Stable	*No data*	*No data*	*No data*	*No data*
Wacker 290 (Wacker Chemie GmbH) VP 1311 (Wacker Chemie GmbH) Wacker 290L (Wacker Chemie GmbH) Rhodorsil X-54802 (Rhone-Poulenc Italia SpA) Degussa WS 405	Some sandstones show moderate increase in compressive strength.	Results variable. Up to 7 cm.	Stable	*No data*	*No data*	Marked reduction in salt damage.	*No data*
RC70 (Rhone-Poulenc Italia SpA) RC80 (Rhone-Poulenc Italia SpA) RC90 (Rhone-Poulenc Italia SpA)	*No data*	*No data*	Stable	*No data*	*No data*	*No data*	*No data*
Rhodorsil 224 (Rhone-Poulenc Italia SpA) Rhodorsil 4673 (Rhone-Poulenc Italia SpA) M.S. Siloxane (HEY'DI) Tegosivin HL-100 (Th. Goldschmidt SA or Tego Italiana Srl) Wacker 090 (Wacker Chemie GmbH) Dialsil C (Texa)	Compressive & tensile strength may be slightly increased.	Results vary from "good" to 7 mm.	Stable	Slight darkening sometimes observed.	*No data*	Marked increase in rate of decay. Spalling of surface observed.	Marked increase in vulnerability.
Neolith 76	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
Hydrogenmethylsiloxane	*No data*	3 mm	*No data*	*No data*	*No data*	*No data*	*No data*
Rhodorsil XR-893 (Rhone-Poulenc Italia SpA) Rhodorsil 10336 (Rhone-Poulenc Italia SpA) Rhodorsil 11309 (Rhone-Poulenc Italia SpA)	*No data*	Up to 7cm.	*No data*	*No data*	*No data*	*No data*	*No data*
Silane modified silica ester	*No data*	5 cm.	*No data*	No effect.	*No data*	*No data*	*No data*

Table A.3 *Data on consolidants and water repellents. Moisture absorption and evaporation, sandstone data & references.*

Product	Effects on strength	Penetration	UV stability	Colour	Abrasion resistance	Salt crystallisation	Frost damage
Baysilone (Bayer)	*No data*	*No data*	*No data*	*No data*	*No data*	Marked reduction in decay rate.	*No data*
BS28 (Wacker Chemie GmbH) & others	*No data*	*No data*	*No data*	*No data*	*No data*	Marked reduction in decay rate.	*No data*
Methylmethacrylate	*No data*	"Very good"	Unstable or stable (refs. differ)	Darkens surface.	*No data*	*No data*	*No data*
Dial PMA (Texa)	*No data*	< 5 mm.	*No data*	Darkens surface.	*No data*	Spalling of surface.	*No data*
Paraloid B-72 (Rohm-Haas)	Modulus of rupture & compressive strength substantially increased. Tensile strength slightly increased.	Poor	*No data*	*No data*	*No data*	Increase in rate of decay.	*No data*
Butylmethacrylate	*No data*	*No data*	Unstable	*No data*	*No data*	*No data*	*No data*
Consolidant 55050 (ARD Raccanello) ARD (Vernici Racanell)	*No data*	*No data*	*No data*	*No data*	*No data*	Increase in rate of decay.	*No data*
Epo-tek 301A (Epoxy Technologies) Araldyt XB2697 (Ciba-Geigy) Araldite AY 103/HY 956 (Ciba-Geigy) & others	Modulus of rupture slightly increased. Little other information.	Up to 10 mm.	Unstable	Large colour changes, darkening & white deposit.	*No data*	*No data*	*No data*
Desmodur N-3390 (Mobay) Phoba 10 (Hispanoquimica SA) Oxanpierre P/529/PIE (Metalfix) & others	Modulus of rupture moderately to greatly increased. Bending strength substantially increased. May be very brittle.	Variable from "very poor" up to 12 cm.	*No data*	Variable from no effect to darkening.	*No data*	Spalling of surface.	*No data*
Organosilicone-modified polyurethane	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
FU 620 W FU 660 W FU 50	*No data*	*No data*	*No data*	Colour changes noted.	*No data*	*No data*	*No data*
Polyfluorourethane + perfluoropolyether copolymer	*No data*	*No data*	Stable	Little or no effect.	*No data*	*No data*	*No data*
Akeogard PF (Syremont) Fomblin YR, Fomblin YU, Fomblin YO4, Fomblin MET (Montefluos or Ausimont SpA)	*No data*	Up to 3 mm (but remains mobile in stone).	Stable	*No data*	*No data*	*No data*	*No data*
(Ausimont)	*No data*	*No data*	Stable	*No data*	*No data*	*No data*	*No data*
(Ausimont & RPE-Carlo Erba Analyticals [ethylenediamide] & Janssen [hexamethylene-diamide]) Fomblin S12 (Ausimont SpA) Akeogard Ba (Syremont)	*No data*	*No data*	Stable	*No data*	*No data*	*No data*	*No data*
Barra fluato (Ital-Barra)	Compressive strength moderately increased.	Poor	*No data*	*No data*	*No data*	Reduced vulnerability to gypsum.	*No data*
Fluoride	*No data*	Poor	*No data*	May cause darkening.	*No data*	*No data*	*No data*
Polyester	*No data*	*No data*	Unstable	*No data*	*No data*	*No data*	*No data*

Product	Effects on strength	Penetration	UV stability	Colour	Abrasion resistance	Salt crystallisation	Frost damage
Stratyl A 228 (Rhone-Progil)	Compressive strength greatly increased.	*No data*	*No data*	*No data*	*No data*	Reduced vulnerability to gypsum.	*No data*
Ca-hydroxide, Ca-carbonate & Portland cement	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
Hexafluoropropene-vinylidene fluoride elastomer	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
Transkote (Sandtex Italiana)	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
Prot-edil	*No data*	*No data*	Unstable	Yellowing	*No data*	*No data*	*No data*

Mixed treatments :

Product	Effects on strength	Penetration	UV stability	Colour	Abrasion resistance	Salt crystallisation	Frost damage
Wacker OH + Wacker 280 (Wacker-Chemie GmbH)	Hardness & strength substantially increased.	4 to 5 mm.	*No data*	*No data*	*No data*	*No data*	*No data*
Paraloid B-72 (Rohm-Haas) + Silicone Dri Film 104 (General Electric)	*No data*	Poor	*No data*	*No data*	*No data*	*No data*	*No data*
Paraloid B-72 + silane (Rohm-Haas)	Modulus of rupture substantially increased.	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
Paraloid B-72 (Rohm-Haas) + Z-6070 (Dow Corning)	Compressive strength substantially increased. Tensile strength slightly increased.	*No data*	*No data*	Little colour change.	*No data*	*No data*	*No data*
Paraloid B-72 (Rohm-Haas) + M.S. Siloxane (HEY'DI)	Compressive strength moderately increased. Tensile strength moderately increased.	Poor	*No data*	*No data*	*No data*	*No data*	*No data*
Araldyt DY022 (Ciba-Geigy) + Dynasil A (Dynamit Nobel)	*No data*	0.5 to 1 cm.	*No data*	Bad white discoloration.	*No data*	*No data*	*No data*

Product	Porosity effects	Water absorption	Water evaporation	Protective efficacy	Application rate	Other notes	Sandstone type	Porosity	References
Wacker OH (Wacker-Chemie GmbH) Conservare OH Stone Strengthener Steinfestiger OH SS-301 (Colcoat Co.) Tegovakon V (Th. Goldschmidt SA) HAS 6 (Colcoat Co.)	Slight reduction of porosity.	Saturation coefficient may substantially reduced. Changes to capillarity.	Both increases & decreases observed.	*No data*	1100-1800 g/m^2	Stable for at least 2 years. Slightly increased linear thermal expansion. Calcite retards condensation.	Wide variety of sandstones with silica, calcite, iron oxide & clay cements.	*No data*	Caro Calatayud *et al.*, 1992; Caselli & Kagi, 1995; De Witte & Bos, 1992; Lukaszewicz *et al.*, 1995; Nishiura, 1995; Pavia Santamaria *et al.*, 1992; Rossi-Manaresi, 1981; Saleh *et al.*, 1992; Snethlage *et al.*, 1989; Valdeon *et al.*, 1992; Wheeler *et al.*, 1992; Zinsmeister *et al.*, 1988
Brethane (Colebrand Pty. Ltd.) Z-6070 (Dow Corning) DF104 (General Electric) & others	*No data*	Greatly reduced.	Substantially reduced.	33-84%	*No data*	Stable for at least 2 years. Slightly decreased linear thermal expansion. Can crack badly on polymerisation at high humidities. Calcite retards condensation.	Variety of sandstones with silica, clay & iron oxide cements.	*No data*	Caselli & Kagi, 1995; Danehey *et al.*, 1992; Price, 1981; Saleh *et al.*, 1992; Santamaria *et al.*, 1995; Wheeler *et al.*, 1992
A1100 (Union Carbide) N2 (Petrarch Systems)	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	Wallace sandstone with siliceous cement.	*No data*	Wheeler *et al.*, 1992
(Petrarch Systems)	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	Wallace sandstone with siliceous cement.	*No data*	Wheeler *et al.*, 1992
Z6030 (Dow Corning) 460 (Mased)	*No data*	*No data*	*No data*	*No data*	*No data*	Relatively short lasting preservation effects.	Wallace sandstone with a siliceous cement & a calcareous sandstone.	*No data*	Rossi-Manaresi, 1981; Wheeler *et al.*, 1992
Wacker H (Wacker Chemie GmbH) Conservare H SS-101 (Colcoat Co.) & others	Slight reduction in porosity.	Results variable but often highly reduced.	Moderately reduced.	*No data*	*No data*	Stable for at least 2 years. Results rather poor after 20 years. Almost total loss of hydrophobisation after 10-15 years. Stable to SO_2 attack.	Wide variety of sandstones with silica, calcite, iron oxide & clay cements.	*No data*	Caselli & Kagi, 1995; Nishiura, 1995; Rossi-Manaresi, 1981; Rossi-Manaresi *et al.*, 1995; Snethlage *et al.*, 1989; Sramek & Kralova, 1981; Wheeler *et al.*, 1992; Zinsmeister *et al.*, 1988
Methyltributoxysilane	*No data*	*No data*	*No data*	*No data*	*No data*	Stable to SO_2 attack.	*No data*	*No data*	Sramek & Kralova, 1981
Wacker 290 (Wacker Chemie GmbH) VP 1311 (Wacker Chemie GmbH) Wacker 290L (Wacker Chemie GmbH) Rhodorsil X-54802 (Rhone-Poulenc Italia SpA) Degussa WS 405	Slight reduction in porosity.	Marked reduction in water absorption & capillarity.	*No data*	45-52%	*No data*	Stable for at least 1 year. Resistant to breakdown by water, salts & acid but not alkalis. Presence of calcite retards condensation. Degussa WS 405 is solvent free system.	Sandstones with calcite & clay cements.	15-35%	Appolonia *et al.*, 1995; Ciabach & Lukaszewicz, 1993; Rossi-Manaresi, 1981; Santamaria *et al.*, 1995; Villegas & Vale, 1992

Product	Porosity effects	Water absorption	Water evaporation	Protective efficacy	Application rate	Other notes	Sandstone type	Porosity	References
RC70 (Rhone-Poulenc Italia SpA) RC80 (Rhone-Poulenc Italia SpA) RC90 (Rhone-Poulenc Italia SpA)	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	Santamaria *et al.*, 1995
Rhodorsil 224 (Rhone-Poulenc Italia SpA) Rhodorsil 4673 (Rhone-Poulenc Italia SpA) M.S. Siloxane (HEY'DI) Tegosivin HL-100 (Th. Goldschmidt SA or Tego Italiana Srl) Wacker 090 (Wacker Chemie GmbH) Dialsil C (Texa)	*No data*	Significantly or greatly reduced. Significantly reduced capillarity.	Greatly reduced.	52-84%	1100-1800 g/m^2	Slightly decreased linear thermal expansion. Generally poor performance. Reduced damage by acid rain in accelerated tests but increased susceptibility to acid mists.	Wide variety of sandstones with silica, calcite, iron oxide & clay cements.	3.5-6%	Angel Bello *et al.*, 1992; Appolonia *et al.*, 1995; Caro Calatayud *et al.*, 1992; De Witte & Bos, 1992; Pavia Santamaria *et al.*, 1992; Saleh *et al.*, 1992; Santamaria *et al.*, 1995; Valdeon *et al.*, 1992; Villegas & Vale, 1992
Neolith 76	*No data*	Reduced	*No data*	*No data*	2-4 L/m^2	*No data*	*No data*	*No data*	*No data*
Hydrogenmethylsiloxane	*No data*	Reduced to close to zero.	*No data*	*No data*	*No data*	Violent release of hydrogen. Bonds well to clays & silica. Ba-hydroxide is added to use up surplus siloxane.	Arkose, quartz 90%, feldspar, kaolinite, calcite, Fe-oxides.	16.70%	Hosek & Sramek, 1992
Rhodorsil XR-893 (Rhone-Poulenc Italia SpA) Rhodorsil 10336 (Rhone-Poulenc Italia SpA) Rhodorsil 11309 (Rhone-Poulenc Italia SpA)	*No data*	*No data*	*No data*	*No data*	*No data*	Good preservation but surface flakes were fragile. After 20 years results varied. Some new decay observed, possibly due to uneven impregnation.	Calcareous sandstone.	*No data*	Rossi-Manaresi, 1981; Rossi-Manaresi *et al.*, 1995; Santamaria *et al.*, 1995
Silane modified silica ester	No significant effect.	Greatly reduced.	Water vapour transmission moderately reduced.	*No data*	5 l/m^2	Reduced decay rate from granular disintegration.	Burgsandstein. Coarse-grained, siliceous cement.	20-25%	Auras, 1993; Sasse *et al.*, 1993
Baysilone (Bayer)	*No data*	Marked reduction in water absorption & capillarity.	*No data*	*No data*	*No data*	*No data*	Calcareous sandstone, Puerto de Santa Maria & Ubeda.	28% & 35%	Villegas & Vale, 1992
BS28 (Wacker Chemie GmbH) & others	*No data*	Marked reduction in water absorption & capillarity.	Water vapour transmission gretly reduced.	*No data*	*No data*	*No data*	Calcareous sandstone, Puerto de Santa Maria & Ubeda.	28% & 35%	Sasse *et al.*, 1993; Villegas & Vale, 1992
Methylmethacrylate	*No data*	*No data*	*No data*	*No data*	*No data*	Degraded by SO_2.	*No data*	*No data*	Clifton, 1984; Horie (1987); Koblischek (1985); Sramek & Kralova, 1981
Dial PMA (Texa)	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	Various calcareous sandstones.	*No data*	Caro Calatayud *et al.*, 1992; Pavia Santamaria *et al.*, 1992

Product	Porosity effects	Water absorption	Water evaporation	Protective efficacy	Application rate	Other notes	Sandstone type	Porosity	References
Paraloid B-72 (Rohm-Haas)	*No data*	Water absorption & capillarity substantially reduced.	*No data*	*No data*	*No data*	Vulnerable to microbial attack. Degrades over time. Slightly decreased linear thermal expansion.	Wallace sandstone with siliceous cement. Various calcareous sandstones.	28% & 35%	Angel Bello *et al.*, 1992; Horie, 1987; Petersen *et al.*, 1993; Saleh *et al.*, 1992; Villegas & Vale, 1992; Wheeler *et al.*, 1992
Butylmethacrylate	*No data*	*No data*	*No data*	*No data*	*No data*	Degraded by SO_2.	*No data*	*No data*	Sramek & Kralova, 1981
Consolidant 55050 (ARD Raccanello) ARD (Vernici Racanell)	*No data*	Reduced water absorption & capillarity.	*No data*	*No data*	*No data*	*No data*	Various calcareous sandstones.	35% & 28%	Angel Bello *et al.*, 1992; Villegas & Vale, 1992
Epo-tek 301A (Epoxy Technologies) Araldyt XB2697 (Ciba-Geigy) Araldite AY 103/HY 956 (Ciba-Geigy) & others	*No data*	Some reduction.	*No data*	*No data*	*No data*	Good preservation but poor penetration. Degraded by SO_2.	Various sandstones with siliceous, calcareous & clay cements.	*No data*	Clifton, 1984; Rossi-Manaresi, 1981; Saleh *et al.*, 1992; Sasse *et al.*, 1993; Sramek & Kralova, 1981; Wheeler *et al.*, 1992
Desmodur N-3390 (Mobay) Phoba 10 (Hispanoquimica SA) Oxanpierre P/529/PIE (Metalfix) & others	No effect (but some effects on water abs./ evap.).	Reduced to greatly reduced	Moderately reduced.	*No data*	Variable up to 6 l/m^2	Reduced decay rate from granular disintegration. May be a lack of consolidation in the outer few mm.	Various sandstones with siliceous, calcareous, ferruginous & clay cements.	20-25%	Auras, 1993; Clifton, 1984; Littmann *et al.*, 1993; Rossi-Manaresi, 1981; Valdeon *et al.*, 1992; Wheeler *et al.*, 1992
Organosilicone-modified polyurethane	*No data*	Initially reduced, less by 1 week. Water vapour adsorption reduced.	Water vapour transmission greatly reduced.	*No data*	*No data*	*No data*	*No data*	*No data*	Sasse *et al.*, 1993
FU 620 W FU 660 W FU 50	*No data*	Marked reduction.	*No data*	Up to 90%	10-150 g/m^2	*No data*	Pietra Serena, calcareous sandstone.	8-8.5%	Guidetti *et al.*, 1992
Polyfluorourethane + perfluoropolyether	*No data*	Greatly reduced.	Moderately reduced.	90%	10-20 g/m^2	*No data*	Pietra Serena, calcareous sandstone.	8-8.5%	Chiavarini *et al.*, 1993
Akeogard PF (Syremont) Fomblin YR, Fomblin YU, Fomblin Y04, Fomblin MET (Montefluos or Ausimont SpA) & others	Moderate reduction.	Varies from little effect to substantial reduction.	Little effect.	From 64% to 85%.	40-90 g/m^2	Effectiveness varied quite widely. Molecular weight varies from 5000 to 8000.	Various sandstones including calcareous & clay cements.	*No data*	Angel Bello *et al.*, 1992; Appolonia *et al.*, 1995; Frediani *et al.*, 1982; Manganelli del Fa' *et al.*, 1981; Piacenti *et al.*, 1985; Piacenti *et al.*, 1992; Rossi-Manaresi, 1981; Tiano *et al.*, 1985
(Ausimont)	*No data*	*No data*	*No data*	75%	40 g/m^2	Molecular weight. 5000.	Pietra Serena, calcareous sandstone.	4 or 7%	Piacenti *et al.*, 1985; Piacenti *et al.*, 1992

Product	Porosity effects	Water absorption	Water evaporation	Protective efficacy	Application rate	Other notes	Sandstone type	Porosity	References
(Ausimont & RPE-Carlo Erba Analyticals [ethylenediamide] & Janssen [hexamethylene-diamide]) Fomblin S12 (Ausimont SpA) Akeogard Ba (Syremont)	*No data*	Marked reduction.	*No data*	50% to 97%.	40-46 g/m^2	Molecular weight 440-5000. Some evaporative loss of lighter molecules. Decline in protective efficacy after 1.5 years.	Pietra Serena, calcareous sandstone. Feldspathic greywacke with carbonate.	3.5-7%	Appolonia *et al.*, 1995; Piacenti *et al.*, 1985; Piacenti *et al.*, 1992; Piacenti *et al.*, 1993a
Barra fluato (Ital-Barra)	Slightly reduced.	Initially reduced, later greatly increased	*No data*	*No data*	*No data*	Very poor performance.	Calcareous sandstone.	*No data*	Rossi-Manaresi, 1981
Fluoride	*No data*	*No data*	*No data*	*No data*	*No data*		*No data*	*No data*	Clifton, 1984
Polyester	*No data*	*No data*	*No data*	*No data*	*No data*	Rapidly degraded by SO_2.	*No data*	*No data*	Sramek & Kralova, 1981
Stratyl A 228 (Rhone-Progil)	Greatly reduced.	Reduced to virtually zero	*No data*	*No data*	*No data*	*No data*	Calcareous sandstone.	*No data*	Rossi-Manaresi, 1981
Ca-hydroxide, carbonate & Portland cement	Reduction in small pores	Significantly reduced.	Virtually unaffected.	*No data*	*No data*	*No data*	Calcareous sandstone.	*No data*	Moropoulou *et al.*, 1992
Hexafluoropropene-vinylidene fluoride	*No data*	*No data*	*No data*	*No data*	*No data*	Used for aggregating decayed stone or joint filling.	*No data*	*No data*	Piacenti *et al.*, 1993b
Transkote (Sandtex Italiana)	*No data*	Greatly reduced.	*No data*	*No data*	*No data*	Some protective effects.	Calcareous sandstone.	*No data*	Rossi-Manaresi, 1981
Prot-edil	*No data*	Greatly reduced.	Some reduction.	*No data*	*No data*	Protection becomes negligible after 2 years.	Pietra Serena, calcareous sandstone.	4 or 7%	Frediani *et al.*, 1982

Mixed treatments :

Product	Porosity effects	Water absorption	Water evaporation	Protective efficacy	Application rate	Other notes	Sandstone type	Porosity	References
Wacker OH + Wacker 280 (Wacker-Chemie GmbH)	*No data*	Substantially reduced.	Moderately reduced.	*No data*	*No data*	Stable for at least 2 years.	Bacchus Marsh sandstone, clay-rich & friable.	*No data*	Caselli & Kagi, 1995
Paraloid B-72 (Rohm-Haas) + Silicone Dri Film 104 (General Electric)	*No data*	*No data*	*No data*	*No data*	*No data*	Still effective, although chemically altered, after 20 years.	Calcareous sandstone. Feldspathic greywacke with carbonate	3.5-6%	Appolonia *et al.*, 1995; Rossi-Manaresi, 1981; Rossi-Manaresi *et al.*, 1995
Paraloid B-72 + silane (Rohm-Haas)	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	Wallace sandstone with siliceous cement.	*No data*	Wheeler *et al.*, 1992
Paraloid B-72 (Rohm-Haas) + Z-6070 (Dow Corning)	None	Substantially reduced.	*No data*	*No data*	*No data*	Slightly decreased linear thermal expansion.	Sandstone from Temple of Karnak, Egypt. : qtz, kao, hem, flsp.	*No data*	Saleh *et al.*, 1992
Paraloid B-72 (Rohm-Haas) + M.S. Siloxane (HEY'DI)	Some near surface blockage.	Moderately reduced.	*No data*	*No data*	*No data*	Slightly decreased linear thermal expansion.	Sandstone from Temple of Karnak, Egypt. : qtz, kao, hem, flsp.	*No data*	Saleh *et al.*, 1992
Araldyt DY022 (Ciba-Geigy) + Dynasil A (Dynamit Nobel)	*No data*	*No data*	*No data*	*No data*	*No data*	Good preservation.	Calcareous sandstone.	*No data*	Rossi-Manaresi, 1981

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GLOSSARY OF TERMS

copolymer:	polymer produced from two or more monomer types.
DP:	degree of polymerisation. Number of times the monomer unit is repeated in the polymer molecule.
Mn:	number average molecular weight. Used when the number of molecules in a sample is being considered (e.g. for chemical reactivity of end groups).
monomer:	chemical units which combine to form a polymer.
M_r:	molecular weight.
MTMOS:	Methyl tri-methoxy silane.
M_w:	weight average molecular weight. Used when weights of molecules are important (e.g. in determining a property such as strength).
oligomer:	small polymer molecules made up from a few monomer units.
PBMA:	polybutyl methacrylate.
PMA:	polymethacrylate.
PMMA:	polymethyl methacrylate.
PVC:	poly(vinyl chloride).
silane:	Basic form is a silicon atom attached to four side groups, e.g. tetra ethoxysilane $(CH_3CH_2O)_4Si$. In the presence of water the molecule polymerises to form silica. Side groups other than alkoxy- may be attached and remain after polymerisation to give the polymer water repellent properties.
siliconate:	Water soluble salts of organo-silicic acids (e.g. potassium methyl silicic acid).
silicon ester:	partially polymerised alkoxysilanes.
siloxane:	Siloxanes contain Si-O-Si bonds and may be formed by partial polymerisation of silanes (oligomer).
T_g:	glass transition temperature. The temperature at which the material turns from glassy to soft.
T_m:	Melting point.