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Factors influencing salt-induced weathering of building sandstone.

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FACTORS INFLUENCING SALT-INDUCED WEATHERING OF BUILDING SANDSTONE

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ABSTRACT

The role of chemical cleaning in causing salt-induced weathering of building sandstone was investigated by looking at the changes in a series of weathering indicators selected. These were mainly, porosity and pore size distribution changes, chemical composition and colour changes.

Laboratory studies involved the use of artificial weathering studies. Samples of Locharbriggs and Crossland Hill sandstones were first studied after partial immersion in salt-contaminated solutions. No temperature variation or humidity cycling was promoted. Samples were then exposed to cycles of humidity and temperature that simulate wet/dry cycles based on field data from a representative Scottish environment. Additional studies involved exposure of samples to SO_2 gas and water spray at acid pH.

These studies aimed at understanding the effects of environmental factors (relative humidity, temperature, SO_2 and pH) which can promote salt-induced weathering of building stone. Weathering studies carried out on chemical cleaned samples have not been reported previously, and therefore represented a novel use of temperature and humidity controlled chambers.

The possibility of environmental/climatic influence on the action of salts in sandstone by means of different intensity on dry/wet cycles, salt crystallisation and salt migration was also studied by exposing the samples to four different locations in Scotland (Banff, rural-coastal; Dunkeld, rural-inland; Aberdeen, urban-coastal and Glasgow, urban-inland) after being chemically cleaned. The analysis of the field exposure data involved statistical analysis and especially multivariate methods of the damage salts against the environmental data.

In general, the indicators selected showed the following trends independently of having a control (not cleaned) or a chemical cleaned sample: porosity decreased, and most ions presented a similar distribution pattern after field exposure.

Keywords: sandstone, salt weathering, stonecleaning, environment, porosity, chemical analysis, colour changes and building conservation.

1 INTRODUCTION

Background

Uncontrolled stonecleaning in the past has caused severe damage to a number sandstone buildings in Scotland (Webster *et al.,* 1992). This together with a lack of understanding of both the immediate and long term effects that stonecleaning treatments can have on stone promoted the funding of a series of research projects. In 1989, the Masonry Conservation Research Group at The Robert Gordon University, initiated a two years project on the subject of stonecleaning and its effects on Scottish sandstones (Webster *et al.*, 1992). This research attempted to determine what effects, both physical and chemical, stonecleaning methods have on building sandstones and what tests should be performed on the sandstone prior to cleaning to determine a stonecleaning method which will not result in excessive damage to the stone. In 1993 and as part of his thesis work, MacDonald (1993) investigated the effects of chemical cleaning processes on sandstone in Scotland. This work highlighted the weaknesses in the understanding of the decay mechanisms associated to chemical cleaning of sandstones.

As a continuation of these works, the Masonry Conservation Research Group and the School of Applied Sciences at The Robert Gordon University in collaboration with Historic Scotland sponsored this research project to investigate the salt-induced weathering mechanisms in chemically cleaned sandstone.

Aims and objectives

This project aims at understanding the mechanisms involved in salt-induced weathering of chemically-treated sandstones within an environmental context. Most studies undertaken in the past have been mainly based on the exposure of small samples of unweathered stone, or studies simulating pollution effects in the laboratory, usually on unweathered stone (Price, 1996).

This work describes experiments designed to allow the study of weathered stones. For this purpose, it was necessary to combine a series of short-term studies investigating the physico-chemical characteristics of the sandstones (mineralogy, porosity, surface analysis, colour measurement, chemical composition) with long-term studies. These included the artificial weathering of stone to accelerate the rate of decay through the application of continuous wetting/drying cycles on sandstones, and field exposure studies to obtain more information regarding the effects of natural weathering environments and also the mechanisms of decay. Weathering studies carried out on chemical cleaned samples has not been reported previously, and therefore represented a novel use of temperature and humidity controlled chambers.

The objectives of this particular project are summarised as follows:

- to relate the susceptibility of the sandstone to cleaning products retention to their mineralogical composition and/or physico-chemical properties (e.g. grain size, porosity, colour).
- to investigate the effects of chemical cleaning processes in the formation of damaging salts by using artificial weathering conditions.
- to investigate the impact of location at four different sites in Scotland in terms of porosity changes, mobilisation or development of salts and colour changes on chemical-cleaned surfaces.
- to determine indicators of the decay process associated with the interaction of chemical-cleaned sandstones (e.g. chemical composition, colour) and the environment (e.g. temperature, rain, wind and SO_2 gas).
- to investigate the possibility of synergism between decay mechanisms on the stone surface such as sulphation (result of polluted environments), salt deposition (chemical cleaning) and/or salt removal (rain pH) by using statistical analysis and especially multivariate methods of the damage salts against the environmental data.

Structure

This thesis is divided into ten chapters. The first two chapters provide a review of the current state-of-the-art on stone decay. An introduction to the concept of stone cleaning is given, together with the main question to be answered in this project: how chemically-cleaned sandstones may develop salt-induced damage. Finally, the second chapter deals exclusively with salt weathering in sandstones and explains the theoretical concepts of salt weathering.

Chapter three describes the methodology selected for the study of the decay indicators (porosity, chemical composition, colour and surface changes) which would provide information on the possible salt-induced decay mechanisms on chemically cleaned sandstone. Also, the development of practical accelerated-ageing tests and correlation between these laboratory tests and field exposure studies are described.

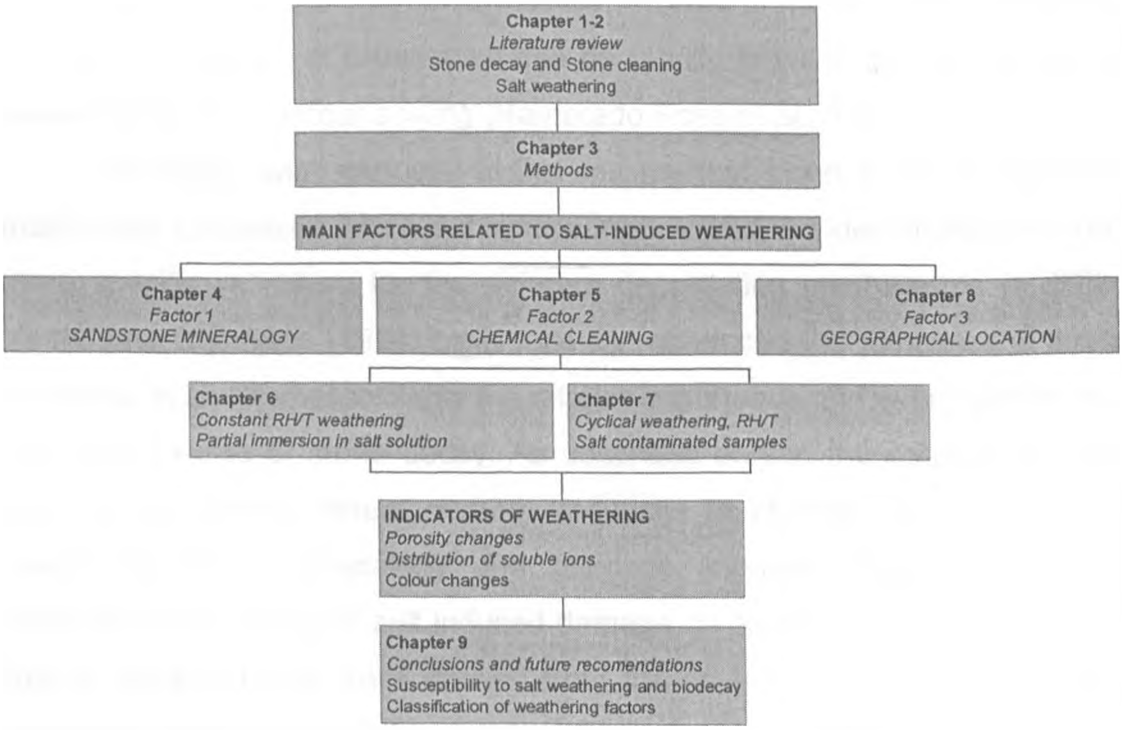
Chapter four briefly describes the sandstones selected for this project; Locharbriggs and Crossland Hill sandstones, including mineralogy and petrography analysis. These stones were selected for this study because of their differences in porosity and mineralogy and also because they are representative in building stone in Scotland. The chapter also presents a prediction of the equilibrium reactions between minerals and cleaning agents.

The results from the study have been divided into four different chapters: Chapter five presents the results on the changes of the decay indicators selected (porosity, chemical composition, colour and surface changes) after chemical cleaning of the two sandstones. In chapter six, chemically-cleaned sandstones were partially immersed in salt solutions of NaCl, Na_2SO_4 and seawater for four months in laboratory studies to investigate the changes in porosity distribution under constant conditions of temperature and humidity. Also, the compression strength was calculated and a theoretical model of compression pressure was adopted to recreate a situation in which the experimental values could be compared with the theoretical ones. Chapter seven includes all the cyclical weathering studies on the chemically-cleaned sandstones. The first study involved the continuous wet/dry cycles on treated sandstones after single immersion in salt solutions of NaCl and Na_2SO_4. Changes on porosity distribution were reported and compared to the ones in Chapter 6 in the final chapter. Additional studies are aimed at understanding the influence of environmental factors (SO_2, pH, relative humidity, temperature) which promote the acceleration of salt formation, which causes damage to stone or creates conditions under which stone decay occurs. These two studies were carried out in the Laboratorio Nacional de Engenharia Civil (LNEC), Lisbon, and focused on the effect of SO_2 gas and acid rain on chemically-cleaned (acid-based) sandstone surfaces.

Finally in Chapter eight, the possibility of environmental/climatic influences on the action of salts in cleaned sandstone (*e.g.* dry/wet cycles, salt crystallisation and salt migration) was investigated by exposing control and cleaned sandstones to four different locations around Scotland: rural-coastal (Banff); rural-inland (Dunkeld); urban-coastal (Aberdeen) and, urban-inland (Glasgow).

The Conclusion chapter draws together the results from previous chapters and develops reactions for evolution of salt-induced weathering in building stone.

General overview of contents



1.1 Stone Decay

The soiling of stone and consequent build up of a patina on the surface, is a result of a combination of different processes. These include the accumulation of soiling derived from external sources such as soot and dust particles, aerosols and gaseous pollutants. The stone surface is also affected by dissolution, alteration and redistribution of minerals within the stone. Also, organisms on and near the stone surface play a part in the development of the patina (Bluck and Porter, 1991).

Sandstone buildings and monuments are subject to both external and internal physico-chemical and biological processes, the interaction of which will depend on the nature of the environment and the degree to which this is affected by both the features of the building and the location of the stone within the building (Bell, 1992).

Natural decay and erosion processes have a damaging effect in their own right. Indeed, through the normal processes of wetting/drying, heating/cooling and freezing/thawing, a natural breakdown of stone, particularly sandstone occurs. These processes can be intensified by salt crystallisation, clay expansion and the internal processes involved in mineralogical conversion. The visual evidence of breakdown can be readily found in surface powdering, delamination and contour scaling (Namorado Rosa *et al.*, 1993).

Generally, once exposed to the environment stone surfaces experience multivariate processes which act simultaneously and the identification of one or more specific indicators for the different degradation mechanisms is difficult. Verdel and Chambon (1994) have recently introduced the principles of system dynamics in an attempt to clarify the relative importance and interdependency of individual causes of stone decay. As described earlier, the causes are varied and include among others: natural variations in climate and environmental conditions, stone mineralogy and previous imposed treatments such as cleaning. In this study of salt induced damage on sandstone, it is hypothesised that in addition to the salts derived from the environment, and those present within the stone fabric, salts may be introduced by chemical cleaning method (i.e. acid based methods) which might cause further damage to the sandstone. This point will be dealt with in more detail in Section 1.2.

There have been several reviews on the causes of stone building decay (Amoroso and Fassina 1983; Bawden, 1985; Winkler, 1994). In general, recent related literature covers three main factors: air pollution, salts and biodeterioration. Considerable attention has been paid to the increased rate of deterioration of historic buildings and monuments related to the effects of atmospheric pollution (Nijs, 1985; Sabbioni and Zappia, 1993; Bell *et al.*, 1995; Moses, 1995; Whalley and Smith, 1995). Price (1996) explains this trend as a consequence of the concerns about the effects of pollution on health, agriculture and the whole global environment. This author describes the many international organisations and institutions funding such research works and also highligths how research into stone building decay has been focused on three main approaches. First, studies on individual buildings coupled with extensive monitoring of pollution levels at their location. Second, studies based on the exposure of small samples of unweathered stone. Third, studies simulating pollution effects in the laboratory, usually on new stone.

Most research has focused on the traditional air pollutants: sulphur oxides, nitrogen oxides and carbon dioxide. All are soluble in water and capable of reacting with calcareous materials such as limestone, marble and sandstone. Although these gases are present naturally in the atmosphere, industrial and human activity has increased their levels, especially in urban areas. For example Halsey (1995) observed an increase in the occurrence of black soiling caused by urbanisation when examining churches of ferruginous sandstone in the west Midlands, England. The author described three forms of weathering which were considered relevant to atmospheric pollution: black soiling, black flaking and black scaling. These weathering forms have been observed in other locations (Fassina, 1992; Steiger *et al.,* 1993; Sabbioni, 1995) and it is suggested that the mechanism of decay is through adsorption of the air pollutants by the stone surface so the pores may ultimately become blocked, trapping moisture behind the crust, which may result in black flaking and scaling.

The formation of gypsum is generally attributed to the sulphation of calcium with atmospheric sulphur oxides (Mangio, 1991) and the presence of non-carbonate particles on the stone surface act as catalyst in the oxidation of SO_2, thus favouring the formation of gypsum (Del Monte *et al.,* 1981). These particles contain metal oxides that catalyse the oxidation process. One formed, gypsum can exert pressure in the pores of the stone by changes in volume, either due to a change in hydration state, cycles of dissolution and re-crystallisation or differential thermal expansion. Gypsum can also assist in the blocking of pores and in the loss of calcium carbonate, which occurs as a natural cementing agent in sandstone (Zehnder, 1993).

Steiger *et al.*, (1993) reported that gypsum is by far the most abundant salt in samples from German monuments. Samples of carbonate or silicate stone were analysed and it was found that in addition to mortar, dry deposition of calcium from the atmosphere should also be considered as a relevant calcium source for the formation of gypsum crusts on silicate sandstones. Gypsum crusts were recorded on calcareous sandstone buildings in Northern Spain. In this case, the main processes that lead to its formation were sulphation of the stone and dissolution of calcite followed by its recrystallisation as sparite, making the stone soft and fragile due to loss of cement (Pavia Santamaria, 1995).

Still there is a need to determine the precise mechanisms on how pollution damages stone. Damage functions are mathematical expressions that attempt to express the rate of stone decay as a function of several different variables. A recent review by Livingston (1996) describes the calculation of these functions and concludes that in most cases, the rate of decay seemed to depend mainly on three factors: pollution levels, rainfall acidity and amount of rainfall.

An important point to address is that even in the absence of air pollution, stone decay occurs. This leads us to the subject of salts. Along with air pollution, soluble salts represent one of the most important causes of stone decay. A through review on the presence, effects and mechanisms of salt-induced decay in sandstone will be discussed in Section 2.

Finally, the deterioration of stone in buildings and monuments through the action of biological processes has been recognised over a long period, but it is only recently that the topic has received increasing attention. There are a number of reviews on the subject, a summary of which can be found in Price

(1994). Most recently, Wakefield and Jones (1998) review the various mechanisms associated with biological decay of building stone.

1.2 Stone Cleaning

Chemical cleaning of masonry has been questioned in the past years for the potential damage it can cause, mainly originating from soluble and insoluble salts left behind in the stone after such treatment. In the United Kingdom, many historic and public buildings have been chemically cleaned (Photo 1.1) but even with the consequential evidence already reported in the literature (Bluck and Porter, 1991; MacDonald *et al.,* 1992; Maxwell, 1992 and Andrew, 1994) indicating that salt induced decay on buildings could be accelerated after such cleaning treatment, the mechanisms of how chemical cleaned sandstones may develop salt induced damage are still unknown.

Research undertaken from 1987 to 1991 indicates that stonecleaning may have benefits to property owners other than purely aesthetic ones and that the public will remain intolerant of soiled buildings (Hamilton *et al.,* 1996). The author continues that in 1990/91 a survey estimated that the UK stonecleaning industry had a value of £79 million.

Today, restoration and conservation of historically significant sandstone buildings is only undertaken after careful consideration of the significance and impact of a cleaning process (Historic Scotland, 1993). Protection for the built heritage is secured through consent systems for scheduled monuments, listed buildings and buildings in conservation areas (Ross, 1997).

Photo1.1 The Usher Hall in Edinburgh was chemically cleaned in 1996.

1.2.1 Chemical cleaning agents

Stonecleaning by chemical methods works by chemical reaction between the cleaning agent, the soiling and the stone surface to which the soiling is attached. Although there is a wide range of chemical cleaning products available commercially, the majority fall into two categories; the acidic and the alkaline cleaners. There are few cleaning products that contain organic solvents (Table 1.1).

Depending on the substrate and type of soiling, the active ingredient in the cleaning product may be a single component or a mixture and can vary in concentration and strength. There is no single acid or alkaline that can be used for all cleaning cases. Commercially, the active ingredients, acid or alkaline, are mixed with relatively inert materials such as gels and poultices which control their viscosity or with active detergents and biocides which help to break up soiling at the surface and kill biological growth (Urquhart *et al.*, 1993).

Hydrofluoric acid is the principal cleaning agent in acidic cleaning products used on sandstone. It is supposed that it works by reacting chemically with the substrate, in particular silicates and then the soiling is removed, along with some dissolved and loosed sandstone, when the surface is washed down with water (MacDonald, 1992). Hydrofluoric acid does not leave leachable salts behind inside the stone but it does however have the potential for depositing insoluble salts (Labrid, 1975).

Alkaline cleaners are commercially available in a variety of chemical formulations, most of them based on sodium hydroxide (NaOH) and less frequently potassium hydroxide (KOH) (Bluck and Porter, 1991; Ashurst, 1994). They work by breaking down (saponification) the organic components of the soiling material on the surface of the sandstone, thus reducing the amount of water needed. Unfortunately, the main disadvantage is their ability to enter and be absorbed into the pore system, leaving soluble residues beneath the stone surface. For example, MacDonald (1992) reported that between 50-70 % of sodium was retained by the stone after the degreasing stage with NaOH.

Table 1.1 Chemical and physical properties of some common chemical cleaning agents (all values refer to dilute aqueous solutions at 25°C)

Chemical	Formula	pKa[1]	ΔG°f (kJ/mol)[2]	Effects
Alkaline cleaning agents				
Sodium hydroxide	$NaOH$	14.8	-418.8	All have the potential for depositing soluble salts within the stone
Potassium hydroxide	KOH		-439.7	
Ammonium hydroxide	NH_4OH	9.25	-236.1	
Sodium carbonate	Na_2CO_3		-1050.6	
Sodium bicarbonate	$NaHCO_3$		-847.9	
Acidic cleaning agents				
Hydrofluoric acid	HF	3.20	-295.1	HF and H_3PO_4 produce insoluble salts. The other acids produce soluble salts
Ammonium bifluoride	NH_4HF_2		-656.8	
Acetic acid	$CH_3(COOH)$			
Hydrochloric acid	HCl		-131.1	
Phosphoric acid	H_3PO_4	2.16 7.21 12.32	-1107.9	
Sulphuric acid	H_2SO_4	1.98	-689.4	

[1] Perrin, D.B., 1982

[2] Lange's Handbook of Chemistry., 1996

1.2.2 Chemical cleaning of sandstones

Chemical cleaning is usually applied when soiling is not water-soluble (i.e. in the case of urban soiling associated to pollution). Bluck and Porter (1991) review the current methods for chemical cleaning of different sandstones. For a siliceous sandstone it will typically involve an alkaline chemical to break the siliceous bonds between the soiling layer and the stone surface followed by a water wash and then an acidic chemical based on hydrofluoric acid (HF), or the acid itself diluted in water. On calcareous sandstone, the alkaline cleaner, usually based on an hydroxide, is used to break down the greasy component of the soiling and undertake the cleaning. This is followed by water washing and then an acidic cleaner based on acetic acid to neutralise the alkaline residues which have not been rinsed out by the water wash.

All acid and alkaline cleaning materials have the potential to cause damage to masonry if used in excessively high concentrations, for excessively long dwell times and without proper pre-wetting and rising procedures. A liquid acid cleaning will generally involve the following steps:

1. Pre-wetting of the stone surface with deionised water to encourage the applied chemical to remain on the surface in contact with the soiling and not to be absorbed into the stone.
2. Application of an alkaline degreaser for an appropriate length of time (*i.e.* between 30-60 minutes).
3. Rinsing with high pressure water spray (typically 600 psi or 4.14 MPa).
4. Application of an acid for neutralisation and further cleaning.
5. Rinsing thoroughly with high pressure water spray.

The danger of some active constituents in chemical cleaning agents, particularly acidic ones, is that they attack some mineralogical constituents of stone, in particular clays and carbonates and therefore dissolve away cementing material leading to a loss of solid material which will result on changes on the surface texture such as preferential erosion and opening of pores. In all cases, it is very important to monitor the method of application, concentrations, dwell times and rinsing regimes. In general, siliceous sandstones are more resistant to hydrofluoric acid than argillaceous or calcareous sandstone due to the clay content and cementing properties (Williams, 1975).

1.2.3 Problems associated with chemical cleaning

In Section 1.2.2, chemical cleaners and their application to stone were described. It was acknowledged that chemical and physical changes may be induced in the stone through the cleaning procedures. Some of these interactions are now described in greater detail in the following sections.

1.2.3.1 Retention of chemicals in sandstone

Porosity and permeability are the main physical factors controlling the transport of water through the sandstone (Meng, 1993) and therefore the factors which influence the potential of cleaning agents to penetrate into the stone matrix. Some sandstones are highly porous and permeable and therefore, chemicals will be introduced in the pore network of the stone regardless of how carefully the sandstone has been washed down after the cleaning process.

Research by MacDonald (1992) showed a tendency for more porous stones to retain a higher proportion of the applied chemicals than less porous stones. In some cases, this proportion accounted for up to 40% to 80% retention of the applied agents for sandstones with porosities of 11% and 20% respectively. His work on freshly cut stone showed that cleaning agents can penetrate into sandstone to depths of up to 20mm. The greatest concentration of retained chemicals generally occurred within 2mm of the surface of the stone and then it decreased progressively with depth.

Research on soiled stones has also shown that absorption of cleaning chemicals can occur, just as in the case of freshly cut stone. However, the subsequent fate of the absorbed chemicals can be affected by the presence of pollutants, or past conservation treatment residues (Fassina, 1995).

Chemical reactions between the cleaning agents and other existing components may result in the formation of additional soluble and insoluble salts in the stone (Section 1.4). For example, sulphate is commonly found in large amounts in aged stone, probably as a result of atmospheric pollution (SO_2) which reacts with rain water to give H_2SO_4 this will readily attack the calcium compounds present in the mortar or the stone to form sparingly soluble calcium sulphate ($CaSO_4$). The application of cleaning agents, NaOH in particular, may result in the solubilisation of this sulphate (MacDonald, 1992).

Once chemicals have gained access to the interior of the stone they will produce short and long term changes in the stone depending on its mineralogical composition, the pollutants present and the nature of the chemical cleaners. Effects may include the precipitation of efflorescence salts on external surfaces, visual changes to the stone colour, such as bleaching or staining and induce colonisation by biological growths (Young, 1997).

1.2.3.2 Efflorescences

Incomplete removal of alkaline cleaning agents may result in the retention of soluble salts. These soluble salts are usually white and manifest clearly on the surface of the stone (efflorescences) or within the stone (subflorescences). Certain salts are prone to effloresce, while others crystallise more readily inside the pore (Rodriguez-Navarro et al., 1996). These authors consider environmental changes, especially relative humidity, as the main factor controlling the location of salt crystallisation.

Salts which are deposited as a result of chemical cleaning will be transported around the stone by continuous wetting and drying cycles. The pressures created within the pores of the stone as a result of continuos hydration/dehydration of salt crystals can cause accelerated decay (Zehnder and Arnold, 1989).

Field observations indicate that efflorescence can be removed by rainwater, but not all building surfaces are reached by falling rain and also the quantity may be insufficient to completely remove the salts (Photo 1.2). Efflorescences will often form on the same surface areas affected by iron staining and soiling accumulation because these are the areas where capillary forces during the wetting-drying cycles have concentrated the soluble ions.

They may also concentrate within clay rich layers in sandstone where they can easily exchange soluble ions and at the mortar (Andrew *et al.*, 1994).

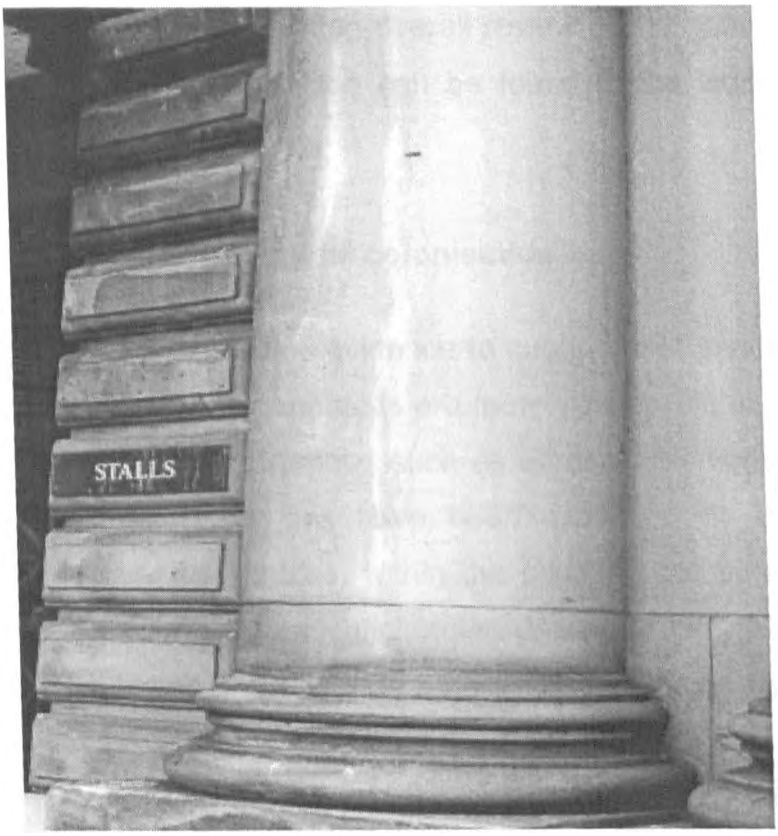


Photo 1.2 Detail of efflorescence on column after chemical cleaning.

1.2.3.3 Colour changes

Cleaning agents may mobilise coloured minerals within the stone, particularly those containing iron and manganese, and cause them to be redeposited at other areas of the stone matrix. Other cleaning agents may dissolve coloured minerals enabling them to be washed out of the stone and cause bleaching of its surface (Andrew at al., 1994). The iron bearing minerals will be dissolved by hydrofluoric acid (HF) and release iron (III) into solution. This ferric iron will precipitate as iron hydroxy but fluoride ion has a great affinity for dissolved iron (III) and therefore the formation of iron fluoride complex will take place over the precipitation of iron hydroxy until pH near 5-6 are reached then migrate to the surface and are deposited as orange or brown stains (Williams, 1975). Also, siliceous minerals (*e.g.* quartz, feldspar and clays) can be dissolved and redeposited on the surface in the form of hard, white, insoluble residues as a consequence of misuse of hydrofluoric acid (Ashurst, 1994).

Another different cause of colour change is biological colonisation. Colonisation of surface by algae or lichens can have a dramatical impact on the aesthetics of a building. An interesting overall review of the principal mechanisms important in stone biodeterioration can be found in the work by Wakefield and Jones (1998).

1.2.3.4 Biological colonisation

There is some evidence to suggest that sandstone buildings cleaned by chemical cleaning methods are more susceptible to algae re-growth than those cleaned by other method such as abrasive methods (Bluck and Porter, 1991). The reasons for this have been explained by the existence of nutrients, especially phosphates, within the cleaning components which are left behind the stone after chemical cleaning (Young, 1998). Also, atmospheric pollutants, particularly nitrates and ammonia may contribute to rapid biological re-growth. (Andrew *et al.*, 1996).

On the other hand, the physical effects of chemical cleaning (removal of surface detritus and opening of pores) provides an increased surface area which may affect water retention and evaporation rates from the stone surface and therefore biological re-growth (Photo 1.3).

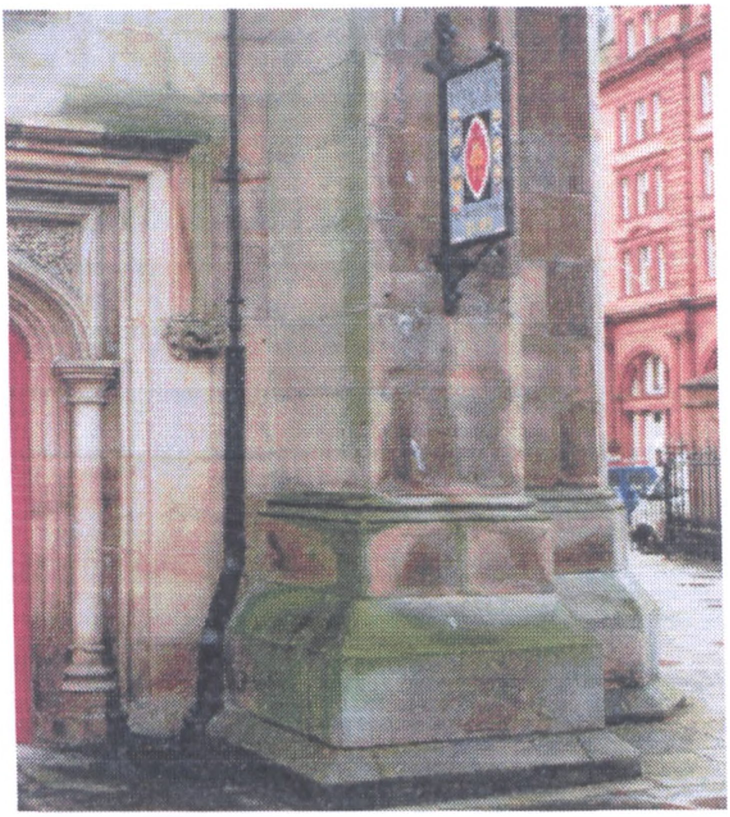


Photo 1.3 Detail of biological colonisation after chemical cleaning at St Mary's Cathedral in Edinburgh.

1.3 Stone characterisation

The degree of resistance that a sandstone offers to weathering depends upon its mineralogical composition, porosity, type and amount of cement, and the presence of any planes of weakness such as lamination (Camuffo, 1995). Accordingly, the best type of sandstone for external use for building purposes is a massive quartz-arenite which is well bonded with siliceous cement and has low porosity (Hammecker, 1995). Sandstones are composed of quartz grains which are highly resistant to weathering, but other minerals present in lesser amounts, for example feldspar may be kaolinized. Sandstones which have calcareous cements are vulnerable to attack even by weak acids. Although the loss of carbonate is relatively very small, it leads to the removal of a large number of grains. The presence of iron oxides, when hydrated, can produce rust strains on the surface of stone. Laminated sandstone usually weathers severely when used in exposed parts of buildings (Ashurst, 1994).

1.4 Chemistry and mechanisms of low-temperature dissolution of silicate rock-forming minerals

1.4.1 Introduction

Reactions involving clay minerals and primary aluminosilicates at ordinary temperatures are very slow and equilibrium cannot be assumed. Wilson (1987) referred to stability diagrams to display equilibrium reactions of different minerals as function of two variables. If only considering the theoretical equilibrium reactions for three of the minerals representing the composition of the sandstones in this project (potash feldspar, $KAlSi_3O_8$; mica, $KAl_3Si_3O_{10}(OH)_2$ and kaolinite, $Al_2Si_2O_5(OH)_4$ then reactions may be written:

Equilibrium 1: K-feldspar

$3KAlSi_3O_8+2H^++12H_2O \leftrightarrow KAl_3Si_3O_{10}(OH)_2+6H_4SiO_4+2K^+$ $\Delta G^0 = 82.7$ kJ/mol

Equilibrium 2: mica

$2\ KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3\ H_2O \leftrightarrow 3\ Al_2Si_2O_5(OH)_4 + 2K^+$ $\Delta G^0 = -56.8$ kJ/mol

Equilibrium 3: kaolinite

$Al_2Si_2O_5(OH)_4 + 5H_2O \leftrightarrow 2Al(OH)_3 + 2\ H_4SiO_4$ $\Delta G^0 = 61.2$ kJ/mol

All equations are written for a slightly acid solution (Wilson, 1987). These equilibrium reactions indicate that feldspar becomes unstable as the solution becomes more acid, changing first into mica and then to kaolinite. Therefore kaolinites would be the expected product of weathering under acidic conditions, observation which is manifested in the natural weathering environments.

The standard free energy change for these reactions were calculated from the equilibrium reactions by subtracting the sum of the ΔG^0 values for the reactants from the sum of ΔG^0 values for the products (Lange's Handbook of Chemistry). ΔG^0 give the standard free energy of formation at 25°C and 1 atm pressure. The relation of free energy change to equilibrium constant for the special case in which all substances are present at unit activity, is expressed as:

$\Delta G^0 = -RT \ln Ka$ (Atkins, 1986)

Therefore to find the equilibrium constant at 25°C:

$\Delta G^0 = -RT \ln K = -1.364 \log K = 82.7$; $K = 10^{-14}$ Equation 1

$\Delta G^0 = -RT \ln K = -1.364 \log K = -56.8$; $K = 10^{10}$ Equation 2

$\Delta G^0 = -RT \ln K = -1.364 \log K = 61.23$; $K = 10^{-10.7}$ Equation 3

The small positive ΔG^0 and the small exponent in K mean that the reactions for feldspars and kaolinite are displaced towards the left but all the substances can exist together in significant amounts at equilibrium. The reaction for mica lead to a negative ΔG^0 and a small exponent in K so the reaction is displaced towards the right.

1.4.2 Mechanisms of low temperature dissolution of silicates

In most natural silicates the chemical bonding between the oxygen of the SiO_4 tetrahedra and elements outside these tetrahedra is essentially ionic.

Feldspars have a 3-dimensional framework of SiO_4 and AlO_4 tetrahedra in which all oxygens of each tetrahedron are shared with the adjacent tetrahedron. Compensation of charges is provided by monovalent cations (Na and K) or bivalent Ca.

Experiments of progressive dissolution on orthoclases (potassium feldspars) and albites (sodic feldspars) (Nahon, 1991) indicated that the reaction doesn't proceed in a uniform manner and that a preferential attack occurs. This author further explained that this preferential dissolution might not be in agreement with the theory of the protective layer according to which surficial and protective coatings assumed to surround feldspars grains would regulate dissolution kinetics but reported dissolution experiments in water reject the existence of this protective coating and even feldspars samples previously etched with HF-H_2SO_4 which would be the case for our studies showed a linear kinetics of the hydrolysis reaction. Therefore under normal conditions of weathering (pH6 and room temperature) feldspars will dissolve without the development of a protective coating that would control this dissolution by diffusion.

Any observed parabolic kinetics would not indicate hypothetical protecting surface layer but would be the result of initial dissolution of fine particles and debris attached to the sample.

Holdren and Speyer (1985) observed that at high pH (i.e. after application of degreaser sodium hydroxide), dissolution of feldspars is not stoichiometric and consists of removal of siliceous residual layers. At pH values close to neutral (i.e. after application of neutraliser hydrofluoric acid), leaching of aluminium is reduced and precipitation reactions decrease the amount of aluminium in solution. Acidic pH would result in preferential release of aluminium and alkaline cations over silica.

In micas, SiO_4 tetrahedra are arranged between a sheet structure of infinite extent. Within this sheet, each tetrahedron shares three oxygens with its neighbour.

Experimental studies on the kinetics of dissolution of micas (Nahon, 1991) were carried out studied at room temperature, in the presence of deionised water and in a closed system with a partial pressure of CO_2 of 1 atmosphere. This author reported that the weight percentage of magnesium and potassium released as a function of time was dependent on the orientation of the hydroxyls which allows a stronger bonding to the structure of interlayer potassium cations in dioctahedral micas than in trioctahedral micas.

Clays have a layered structure composed of two structural units, a silica sheet and an alumina sheet (Figure 1.1). In studies of aluminosilicate mineral (clay and feldspar) dissolution, Labrid (1975) concluded that HF uniformly attacks the clay structure solubilizing both silicon and aluminium. However, in the later stages of reaction, aluminium dissolution continues while silica is precipitated from solution in the form of colloidal silica.

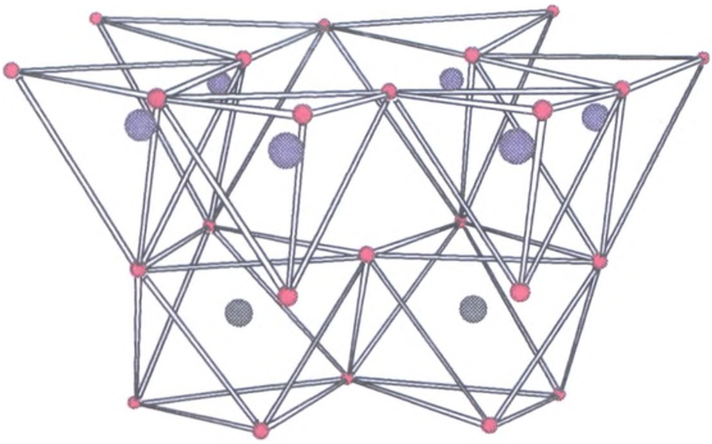


Figure 1.3 3D structure of kaolinite. Tetrahedra structures are joined by oxygen atoms (red); silicon (purple) and aluminium (grey) atoms stay in the center.

Beneth and Casey (1996) explained the dissolution of minerals considering there are three sequential steps to removing a metal from a dissolving mineral surface. First, reactive solutes (H or OH) must migrate through the aqueous solution to the mineral surface. Second, the solutes combine with metals to form the reaction product which desorb. Third, the dissolved product diffuse away from the mineral surface along concentration gradients. The slowest of these three sequential processes controls the rate of the overall dissolution reaction. These authors considered the second step as the rate-determining step. In experiments with feldspar in acid, aluminium, calcium and sodium were leached away from the near-surface region leaving a silica rich surface.

If considering the hypothesis that the reactions which remove a metal from a mineral surface have much in common with the reactions that replace ligands around a dissolved metal (Beneth and Casey, 1996) then for example in the case of hematite, continued replacement of surface-bridging oxygens with coordinated water molecules releases the $Fe(H_2O)_6^{3+}$ into solution and dissolution occurs. On the other hand, when there is a change in coordination number between the oxide and the ion then large variations between solution and surface properties are observed. For example, silicon is tetrahedrically coordinated as silicic acid and in most rock-forming silicates but it is octahedrally coordinated in aqueous solutions by fluoride (SiF_6^{-2}).

Therefore, the coordination chemistry of chelated metals is an important consideration when looking at the initial mechanisms of dissolution and decay of sandstones.

Metals on the surface of silicate minerals are also connected by oxide or hydroxide ion bridges which undergo acid-base reactions in the aqueous solution. The enhancement of dissolution rates via adsorption of hydrogen ions is referred to as the proton-promoted pathway for dissolution (Beneth and Casey, 1996). These authors considered the acid-base chemistry of a particular mineral surface as a characteristic of its composition and structure just as the hydrolysis chemistry of a particular dissolved metal. In general, the slow dissolution kinetics is enhanced by rapid adsorption reactions and this process varies with pH. As the anionic character of a surface increases cation sorption is selected over anion sorption.

Acid penetration into sandstone after HF treatment is primarily controlled by the chemical composition of minerals the acid contacts and not by the average composition (Williams, 1975). Reaction rate of HF with silicate minerals (clays, feldspars or micas) is much more rapid than with silica, and if these highly reactive minerals are present in large percentage than acid then this will not penetrate deeply into the stone. However, a high clay content does not necessarily indicate that acid penetration is restricted. When clays are uniformly distributed they will be contacted with acid. If clays simply fill the pore space of the sandstone then the acid will selectively bypass the pore network. For samples with a low clay content (less than 10%), the clay is often uniformly dispersed and available for reaction. Acid often channels through the larger pores and the assumption of uniform contact is normally not valid (Williams, 1975).

Clays will react with HF to form silicon and aluminium fluorides according to the simplified reaction proposed by Brosset (1943):

$$Al_2Si_2O_5(OH)_4 + 18HF \xleftrightarrow{H_2O} 2H_2SiF_6 + 2AlF_3 + 9H_2O$$

This author also suggested that normally a distribution of reaction products will coexist, the silicon fluorides as SiF_4, SiF_5^- and $SiF_6^=$ while aluminium fluorides as Al^{3+}, AlF^{2+} until AlF_6^{3-}. The presence of illite clay would also make possible the precipitation of potassium fluorosilicate (K_2SiF_6) instead of silica $Si(OH)_4$.

2 SALT WEATHERING OF SANDSTONES

2.1 The Presence of Salts in Sandstone

The presence of salts in the pore water of sandstone give rise to different effects. One effect is efflorescence, which is salt crystallisation on the surface of the stone. Efflorescences consist of water-soluble salts that initially may have been present in the sandstone or may have formed as a result of reactions of atmospheric gases with materials in the stone. Commonly occurring efflorescences may contain potentially harmful salts as sulphates of calcium (Ca), magnesium (Mg) and sodium (Na) (Arnold, 1976). These kind of salts and other soluble salts such as halite (NaCl) and niter ($NaNO_3$) can also be associated with the disaggregation and alveolisation of stone on monuments (Hammecker, 1995). In the lower part of buildings, more susceptible to capillary rise of water, soluble salts sometimes crystallise in the pore network of the stone, provoking internal stress and disaggregation. In subflorescences, crystallisation takes place just below the surface of the stone, the outer skin frequently losing its support and exfoliation occurs. Again calcium and magnesium sulphates are among the most common salts involved (Winkler, 1994). This author gives examples of salts that were commonly observed as efflorescence on sandstone (Table 2.1).

Table 2.1 Salts found as efflorescence in sandstone (Winkler, 1994)

Chemical-Composition and Mineralogy	**Chemical Name**	**Solubility (H_2O) 20°C, g/ml**
Na_2CO_3 (soda ash)	Sodium carbonate	16
$Na_2CO_3 . 7H_2O$ (natron)	Sodium carbonate decahydrate	17
$CaSO_4$ (anydrite)	Calcium sulphate	2
$CaSO_4. 2H_2O$ (gypsum)	Hydrated calcium sulphate	2
$CaCl_2 . 6H_2O$ (ice-foe)	Calcium chloride hydrate	279
$MgSO_4$ (kieserite)	Magnesium sulphate	26
$MgSO_4.7H_2O$ (hepsomite)	Magnesium sulphate heptahydrate	71
$MgCl_2 . 6H_2O$ (bischofite)	Magnesium chloride hexahydrate	167
Na_2SO_4 (thernadite)	Sodium sulphate	4.8
$Na_2SO_4 . 7H_2O$	Sodium sulphate heptahydrate	20
$Na_2SO_4 10H_2O$ (mirabilite)	Sodium sulphate decahydrate	11
NaCl (halite)	Sodium chloride	36
$NaNO_3$ (nitratine)	Sodium nitrate	91

Variations in temperature, pressure and water content within masonry contribute to the complexity of salt weathering (Knofel *et al.*, 1984; Rodriguez-Navarro *et al.,* 1996). In addition, salt weathering may be complicated by differences between solubilities and crystal growth behaviours of different salts (Burgess-Dean, 1994). Potassium and other alkali chloride may be formed by displacement reactions within the sandstone. Potentially, the most damaging salts are those that can hydrate. Hydration of such salts causes expansion and crystal growth within the pore structure of the stone (Zehnder and Arnold, 1989). For example, chlorides of calcium and magnesium were observed to cause significant deterioration to sandstone (Lewin, 1983).

Spry (1990) suggested how as stone weathers, chemical displacement reactions occur such that low solubility stable salts such as sulphates and carbonates can be converted into more damaging hydrated sulphates and carbonates. The classes of salt change from A→B→C→D, where A represents the most stable low solubility salts and D the more damaging deliquescent hydrous salts are illustrated in Table 2.2. This author suggests the type of salt that is present in the stone may determine the degree of salt weathering. However, over time the magnitude of deterioration may increase due to the possible formation of more damaging salts.

Table 2.2 Classes of Salt Types in Ascending Order of Capacity to Cause Deterioration (Spry, 1990).

CLASS	SALTS
A: Low solubility stable salts	$CaCO_3$, $CaSO_4$
B: Anhydrous stable salts	NaCl, $NaNO_3$, KCl, KNO_3, K_2SO_4, K_2CO_3
C: Efflorescences hydrous salts	$Na_2SO_4.nH_2O$, $MgSO_4.nH_2O$, $Na_2CO_3.nH_2O$.
D: Deliquescent Hydrous salts	$CaCl_2.nH_2O$, $MgCl_2nH_2O$, $Ca(NO_3)_2.nH_2O$, $Mg(NO_3)_2.nH_2O$

2.2 Sources of Salts in Sandstones

Natural sandstone contains soluble salts such as sulphates and chlorites which are the weathering product of mineral components. Most ferric hydroxide deposits on the surface of sandstones originates from the iron contained in pyrite. Groundwater will also contribute to the presence of many these soluble salts, especially sulphates, chlorides and nitrates. Calcium may be contained within the stone, derived from the mortar surrounding the stone or from dry deposition (Smith *et al.*, 1993). In areas of high pollution, the acidic sulphur content in rain may result in the formation of gypsum (Sabbioni and Zappia, 1991). Atmospheric sulphur dioxide in Scottish urban areas compares closely with data from the UK Review Group on Acid Rain (UKRGAR, 1990) who found levels of about 9-30 $\mu g/m^3$.

Sodium chloride is prevalent in sandstone structures that are situated in coastal regions (Moropolou *et al.*, 1995). Large amounts of sodium chloride may accumulate in the outer surface of masonry due to absorption of sea spray that contains high concentrations of the salt (Winkler, 1994).

In coastal locations, the presence of sea salt accelerates stone decay by crystallisation (Zezza and Macri, 1995). However, this salt also enhances the uptake of sulphur dioxide from polluted air by increasing the time for which stone surfaces retain moisture, and hence the rate of decay even further when both pollutants are present together (Cooke and Gibbs, 1991).

Sea salt aerosols (mostly sodium and magnesium chlorides) are deposited "dry" and "wet" throughout the United Kingdom, but their stronger concentrations are near coasts (Stevenson, 1968; Martin and Barber, 1978; UKRGAR, 1990). These authors reported that inland concentrations are related to wind strength and most of the annual deposition in an inland area arises from a few days of high winds. Deposition of marine salts on stone surfaces can be caused by marine (splash and spray by seawater directly) or atmospheric processes (washout and dry fallout) (Winkler, 1994). Dollard *et al.*, (1983) in a study of the deposition of atmospheric pollutants in Northwest England, reported on the importance of wind-driven mist and fog to explain the increase observed rates of wet deposition by up to 20%. Vale's data (Vale, 1991) also permit analysis of deposition patterns on shorter timescales. Within the 1989 annual total, 70% of deposition occurred within one two-week sample period. Vale states that high chlorine concentrations are associated with westerly winds and that episodic high chlorine deposition rates probably result from the combination of westerly gales together with rainfall. Marine deposition by splash and spray is likely to be most effective during storm conditions and is also an episodic process.

The presence of plants and animals in sandstone may also enhance the formation of salt in building structures. Inorganic ions that were by-products of micro-organism metabolism may leach through the porous structure of sandstone. Bacteria and fungi also have been thought to cause the conversion of salts from less aggressive to more damaging forms in weathered stone (Winkler, 1994). However, proof of this has yet to be reported. In addition to the salts derived from the environment, and those present within the stone fabric, salts may be introduced by selected chemical cleaning methods such as acid based methods and this might cause further damage to the sandstone (Fassina, 1995).

2.3 Salt Weathering of Sandstones

The most important damage processes are associated with the crystallisation of salts within the pores of the stone, this damage arises, in most cases, from moisture migration phenomena (Meng, 1993). For example, salt attack only happens when a high moisture content and a mass transfer process permit solution, migration and crystallisation of soluble salts (Snethlage and Wendler, 1997; Garrecht *et al.*, 1991; Goudie, 1995).

Crystallisation of salts within the pores of the stone has been recognised as the principal cause of stone decay in urban environments in the UK (Lewin, 1982; Sperling and Cooke, 1985; Goudie, 1986; Bell, 1992). Crystallisation caused by freely soluble salts such as sodium chloride or sodium sulphate normally leads to the surface of the stone crumbling or powdering (Photo 2.1). Salt action can give rise to honeycomb weathering in sandstones (Mustoe,

1982) (Photo 2.2). Disruption in stone also may take place due to considerable contrasts in thermal expansion of salts in the pores (Macias *et al.*, 1993).

The deterioration caused by soluble salts that can crystallise, either as hydrates or anhydrates, was investigated by Charola and Weber (1993). Sodium sulphate, which can crystallise as the decahydrate mirabilite (Na_2SO_4 $10H_2O$), or the anhydrous themadite (Na_2SO_4), is known to cause greater deterioration and at a much faster rate than a non-hydrating salt such as sodium chloride. It is still not clear whether the increased damage this salt produces is due to the crystallisation process or to the hydration of the salt although recent work by Doehne (1998) using environmental scanning microscopy showed no damage from sodium sulphate due to hydration.

Transport of salts from the inside of porous sandstone to the surface may give rise to the formation of a case hardened outer crust. Such crusts may act as protective coating if composed of secondary calcite or calcium sulphite. Superficial induration is temporary if the stone is the sole supplier of the salts for the outer crust. At the same time the internal structure of the stone is weakened. It has been known for some sandstones to be largely deprived of their internal cement so that once the case hardening is removed the stone crumbles and collapses (Winkler, 1994).

Frost can also affect salts within the sandstone leading to stone decay. Research by Williams and Robinson (1981) showed that, under laboratory experimental conditions, freezing and thawing cycles of sandstones containing sodium chloride and sodium sulphate resulted in the almost complete disintegration of some sandstones types. Salts cause freezing to take place more slowly, allowing a longer time for larger more damaging crystals to grow in the pore spaces of the stone.

Most sandstones resist frost action and in temperate climates such as found in Britain, frost damage is not a serious problem. However, where rain and snow can collect, such as on copings and cornices so that they remain very wet for significant periods, the stone may be attacked by aggressive cycles of freeze/thaw activity (Hudec, 1991). On the other hand even susceptible stones may not be damaged when they are placed in a sheltered location. The reason why most sandstones are more or less immune to frost damage is mainly due to their pore size which is largely greater than > 20 nm. These are mostly above the critical pore size for freeze-thaw durability about 5 nm. (Hudec, 1991).

(A)

(B)

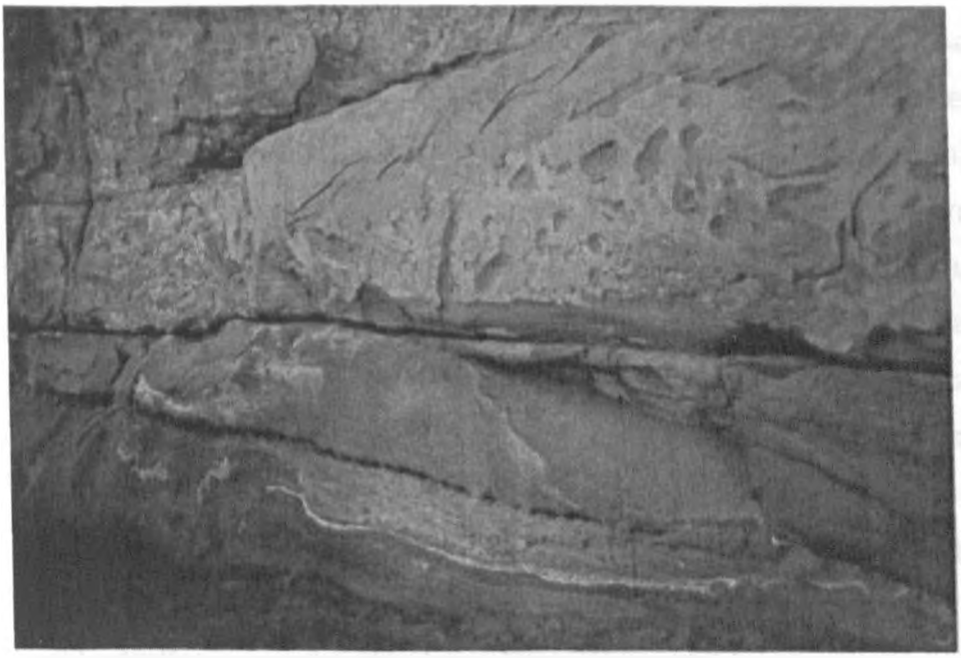


Photo 2.1a-b Examples of salt damage to sandstone; (A) stone powdering from ornament at Standford University (USA) and (B) intensive honeycomb at Mesa Verde (USA).

A strategy to develop an appropriate methodology for determining the possible salt induced decay mechanisms on cleaned sandstone involves an understanding of decay mechanisms, selection and measurement of decay indicators, the development of practical accelerated-aging tests and correlation between laboratory tests and natural weathering (Searls and Thomasen, 1990). Evans (1970) was the first to make any significant association between the deformation of natural rock and stone and the observed deterioration of building stone. Since then, many authors have reported that salt weathering resembles deformation that is caused to rock and stone due to salt crystallisation (Sperling and Cooke, 1985; Binda and Baronio, 1987; Bortz *et al.*, 1993; Goudie and Viles, 1995). A discussion follows that aims to provide an explanation of the processes that are involved during salt weathering.

2.4 Theoretical Concepts of Salt Weathering

Salt weathering has been attributed to the physico-chemical processes that occur when a salt crystallises within the porous structure of stones (Evans, 1970). Many authors have considered that salt crystallisation is the dominant process that deforms rock, stone and building materials during salt weathering (Sperling and Cooke, 1985; Zehnder and Arnold, 1989 and Winkler, 1994). This damage arises, in most cases, from moisture migration phenomena (Garrecht *et al.*, 1991; Goudie, 1995; Snethlage and Wendler, 1997; Theoulakis and Moropoulou, 1997). A general review of the problem of salt damage can be found in the monograph by Goudie and Viles (1997). In general, as reported by Rodriguez-Navarro and Doehne (1998), it is widely accepted that salts cause more damage to rocks containing large proportion of micropores connected to macropores. Still there is a lack of experimental observations as to where and how salts grow in porous materials. Other physical effects such as hygroscopic expansion, capillary pore pressure, chemical dissolution, thermal expansion, and hydration pressure also have been observed to occur simultaneously during salt crystallisation (MacGreevy, 1985; Sperling and Cooke, 1985; Young, 1987; Arnold and Zehnder, 1990; Doehne, 1994; Mottershead and Pye, 1994; Winkler, 1994).

2.4.1 Force of Crystallisation and Pressure Solution

The phenomena of the force of crystallisation and pressure solution are processes that initiate dissolution of a solid phase through a thin film of solution in a solid-liquid contact zone. Weyl (1959) has discussed the necessary conditions of shear and normal stress that are required in thin films to sustain a crystallisation force or pressure solution on the surface of a crystalline material. In deriving his model, Weyl (1959) presented no experimental evidence but based his theory on phenomenological arguments of thin films involved during salt weathering and sedimentation of rock formations. Later on, Lehner (1992) introduced non-equilibrium thermodynamics to define pressure solution. Using this theoretical approach, Lehner (1992) was able to extract kinetic data about the rate of mass transfer away from a stressed solid. However, Correns (1949) provided a theoretical treatise of the force of crystallisation or crystallisation "pressure" for an isothermal, adiabatic system. This theory has been accepted by many authors to explain how crystallising salt may impose stress to stone.

By applying the Riecke Principle[1], Correns (1949) derived a classical, thermodynamical relationship for the crystallisation pressure of a growing crystal. The relationship is shown in equation (2.1). If it is assumed that a crystal will nucleate and grow in a supersaturated liquid solution, from equation (2.1), the crystallisation pressure can be defined as that pressure which will prevent the nucleation and growth of the solid phase. Alternatively, the crystallisation pressure can be defined as the pressure required to transform a supersaturated liquid solution, adiabatically and reversibly into a saturated solution (Correns, 1949). Equation (2.1) also indicates that crystallisation pressure is inversely proportional to the molar volume (of a solid crystal) but proportional to the degree of supersaturation on the surface of that crystal.

---

[1] The Riecke principal states that a crystal under linear stress has a lower melting point, or a greater solubility than an unstressed crystal.

$$Pc = \frac{NkT}{\Delta \nu} \ln \frac{C}{Cs} \qquad (2.1)$$

where:

Pc	is the crystallisation pressure (N/m^2)
C	is the actual concentration of solute (mole/m^3)
Cs	is the equilibrium concentrations of solute (mole/m^3)
v	is the molar volume (m^3/mol)
T	is the thermodynamic melting point (K)
N	is Avogadros number
k	is the Boltzmann constant

According to equation (2.1) a crystallisation force arises due to a local supersaturation of a solute in a stressed aqueous solution in the contact region between two solid surfaces. This local supersaturation provides the driving force for crystal growth of the solute's crystal surface and may result in mechanical fracture of rock and porous building materials (Knofel *et al.*, 1984; Binda and Baronio, 1987).

Disregarding any inadequacies of the theory, Singer and Winkler (1972) calculated the crystallisation pressures of some common salts using the relationship given in equation (2.1). The calculated pressures are very large and in themselves may cause enough stress to exceed the tensile strength of sandstone and many rocks (Knofel *et al.,* 1984). However, it was suggested by the same author that it was improbable that the supersaturation ratio of soluble salts in sandstone exceeded 2. This suggests that catastrophic fracture that is experienced during salt weathering of sandstone may not solely occur by a mechanically induced fracture. There must be another process similar for a force of crystallisation process which leads to the alteration of the pore structure of sandstone during salt weathering. It may follow that crack initiation and propagation may be enhanced to an extent that mechanical fracture by a crystallisation force becomes more likely.

2.4.2 *Hydration Pressure*

Some salts have the ability to absorb water into their structure which changes the lattice parameters to form a new crystal (Brodale and Giauqe, 1957). The addition of waters of crystallisation often causes an increase in the molar volume of the salt and a change in crystal structure. It has been proposed by many authors that the expansion of a crystal due to hydration causes a so called "hydration pressure" which is imposed to the surroundings (Sperling and Cooke, 1985; Charola and Weber, 1993; Doehne, 1994). The relationship in equation (2.2) shows the capacity of hydrous salts to develop a hydrostatic pressure in their surroundings during the diffusion limited absorption of water into their crystal lattices (Winkler and Wilhelm, 1970). Equation (2.2) is analogous to equation (2.1) in that the derived pressure is inversely proportional to the molar volume of the phase change. In the case of a hydration pressure, the supersaturation ratio is replaced by a ratio of vapour pressure at the surface of a hydrating crystal to atmospheric pressure.

$$P_H = \frac{NkT}{\Delta v} \ln \frac{P_{H_2O}}{Pa} \qquad (2.2)$$

where:

P_H is the hydration pressure (kPa)
P_{H_2O} is the vapour pressure of water at the solution surface (kPa)
P_a is the atmospheric pressure (kPa)
Δv is the change in molar volume (m^3/mol)
T is the system's temperature (K)
N,k is as defined in equation (1)

Equation (2.2) represents the formation of a hydration pressure in adiabatic and isothermal conditions. According to equation (2.2) the driving force for salt hydration is the ratio of dislocation pressure to atmospheric pressure (dislocation vapour pressure is the pressure of aqueous vapour in equilibrium with two salt hydrates or with an anhydrous salt and a hydrate) (Sperling and Cooke, 1985). Therefore, a hydration pressure is developed when the vapour pressure on the surface of hydrating crystals is greater than the dislocation pressure of the salt-salt hydrate system.

2.4.3 Capillary Pressure

In the porous structure of sandstone, a change in the volume of solution during crystal growth may also cause stresses to develop due to changes in surface tension at regions of contact between crystals and stone (Theoulakis and Moropoulou, 1997). The inconsistency of pore size within sandstone could be critical to how much stress is developed due to surface tension effects during the crystal growth of a salt (Camuffo, 1995). Nucleation is most likely to occur first in coarse pores (>10μm) of stone (Rossi-Manaresi and Tucci, 1991). The saturated solution in smaller pores (<10μm) then serve as a reservoir for growth of these crystals. A change in surface tensions in the liquid phase causes a pressure to develop that is referred to as a capillary pressure. Wellman and Wilson (1965) concluded that salt crystallisation will take place initially in the larger pores from solution being supplied from the smaller capillaries. When the larger capillaries are filled the thermodynamically preferred process is to continue growing in the large pores and therefore generating pressure that can exceeds the strength of the porous material. Wellman and Wilson (1968) proposed that the excess pressure, P (in atmospheres) built up in a large pore when crystallisation takes place is equal:

$$P = 2\sigma\,(1 / R - 1 / r) \qquad (2.3)$$

In Equation (2.3) σ is the surface tension of the solution and r and R are the radii of small pores and coarse pores respectively. The calculated pressure P, is an excess of the pressure built up when crystallisation proceeds from a coarse pore to a smaller, interconnected one.

2.5 Salt Crystallisation within Sandstone

Lewin (1982) attempted to describe salt crystallisation within masonry as a balance between the migration of a salt solution through the pores of the structure and the evaporation of this solution at the surface of the sandstone.

Lewin (1982) stated when the rate of evaporation is slower than the rate of replenishment, a dry zone forms (usually at or just beneath a normally exposed surface of clay masonry) in which crystallisation of the salt occurs. This theoretical relationship, delineated by equation (2.4), established the necessary conditions for salt crystallisation to occur within the pores, cracks and channels at and beneath an exposed surface of masonry.

$$d = \frac{8F_s D\eta L(P_s - P_a)(Mr / NkT)}{F_p\rho F_w\pi R4\left[\frac{2\sigma\cos\theta}{r}\right] - h\rho g} \qquad (2.4)$$

where:

d	is the diffusion layer thickness (m)
F_s	is the surface porosity
F_p	is the fractional area of masonry with contributing porosity
F_w	is the fractional mass of water in solution
D	is the diffusion coefficient
η	is the viscosity (Ns/m^2)
L	is the total length of capillary network in which solution flows (m)
P_s	is the vapour pressure of water at solution surface (kPa)
P_a	is the atmospheric pressure (kPa)
Mr	is the molecular mass of the solution (g/mol)
N	is the Avogadros Number (atom/mol)
k	is the Boltzmann constant (J/K)
T	is the Temperature (K)
ρ	is the solution density (kg/m^3)
π	is the numerical constant
R	is the Poiselle radius (m^3)
r	is the Laplace radius (m^3)
σ	is the surface tension (N/m)
θ	is the solution contact angle with the masonry (°)
g	is the gravitational constant (m/s^2)
h	is the height solution is above the base of the masonry sample (m)

Equation (2.4) indicates that the theoretical driving force for crystallisation was due to (a) the characteristics of the solution including density, viscosity, concentration, vapour pressure, surface tension, diffusivity and molar mass, and (b) environmental factors, including temperature, relative humidity and air pressure. Unfortunately, the level of experimental error quoted by Lewin (1982) was of the same order of magnitude as the result. Therefore, the accuracy of Lewin's theoretical relationship given in equation (2.4) can only be regarded as an approximation of actual crystallisation of salt stone.

In conclusion, there are still many unexplained differences regarding the crystal morphology, crystallisation patterns, kinetics and substrate damage, for example when comparing salt damage by mirabilite and thernadite versus halite (NaCl). Recent work by Rodriguez-Navarro and Doehne (1998) exposed some of the weaknesses in the previous works and conclude that salt damage due to crystallisation pressure appears to be largely a function of solution supersaturation ratio and location of crystallisation. These factors are related to solution properties and evaporation rates which are controlled by solution composition, environmental conditions, substrate properties and salt crystallisation growth patterns.

The theories supporting the dependence between susceptibility of the porous stone to salt decay and the mechanical and structural parameters of the stone (pore size distribution and compressive strength) have been widely accepted (Correns, 1949, Fitzner and Snethlage, 1982; Camuffo, 1995) and they conclude that salt decay occurs only when optimum porosity characteristic are obtained (Rossi-Manaresi and Tucci, 1991) and the pressure exerted by a growing crystal in a pore is a function of the supersaturation ratio (Correns, 1949).

2.6 Salt Weathering Simulation

A large number of laboratory simulations have now been undertaken to assess the power of salt crystallisation, salt hydration and the thermal expansion of salt and to investigate the role of rock properties, salt types and concentrations (Perez *et al.*, 1995; Goudie and Viles, 1995; Skoulikidis, 1995) (see Table 2.3).

From the examples showed in Table 2.3, samples have been repeatedly immersed in saturated salt solutions, or subjected to continuous partial immersion. This approach does not consider the effects of daily cycling of atmospheric temperature and humidity that is crucial in causing changes in the state of salt in rock pores and cracks, which in turn promote rock disintegration (Goudie, 1993).

Table 2.3 Some previous methods of salt weathering simulation.

Study	Method of measuring change	Treatment
Sperling and Cooke (1985)	Loss weight	(i) Continuos immersion in saturated solutions (ii) One initial immersion cycle
Pye and Sperling (1983)	Grain size change	Continuous immersion in saturated solutions
Kwaad (1970)	Weight loss and grain size change	Continuous partial immersion in saturated solutions
Cooke (1979)	Weight loss and degree of splitting	Cyclic immersion in saturated solutions
Jerwood *et al.* (1990a)	Weight loss and particle size change	Continuous immersion in miscellaneous salt concentration
Smith and McGreevy (1988)	Visual appraisal of surface desegregation	One initial immersion cycle in miscellaneous salt concentration
Fahey (1985)	Changes in particle size	Low salt concentration, 0.2M. Partial immersion
Goudie (1986)	Weight loss and particle size change	Continuous immersion with salts of miscellaneous concentrations
Goudie (1974)	Weight loss	Cyclic immersion in saturated solutions

Adapted from Goudie (1993)

The mechanisms responsible for the deterioration of natural stone are very complex, with several interactions taking place at the same time (physical, chemical and biological). It is assumed that these interactions do not follow the principle of superposition and differ from stone to stone. Riecken and Schwamborn (1995) described a new experimental apparatus called VENUS, used for accelerated, reproducible and complex weathering. Acceleration is achieved by selecting those parameters which are most important for the deterioration and then, combined in a special way to form a cycle.

Other simpler approaches make use of environmental cabinets programmed to give cycles of temperature and humidity. Blocks of rock are immersed for 24 hours in saturated salt solutions and the amount of salt taken up is measured (by weight change). Salt weathering can be caused by daily cycles of temperature and humidity following a single immersion. It is not necessary for repeated immersion to be employed for breakdown to occur. Also, different climatic conditions will create differing degrees of breakdown (Doehne, 1994).

In all cases, the evaluation of the resulting damage after salt weathering simulation is referred as total weight loss (Goudie, 1993). Further information can be obtained by monitoring the changes in porosity and pore size distribution, as well as the distribution of salts in the decayed stone (Rodriguez-Navarro and Doehne, 1998). These authors recently investigated the damage caused by sodium chloride and sodium sulphate in limestone by using an environmental scanning microscope. This new tool allows the direct observation of the process of dissolution and precipitation of salts in porous substrates.

3 METHODS AND MATERIALS

3.1 Investigation programme

The investigation programme followed as part of this research work was divided into three different stages. The first stage involved selection and identification of the sandstone and chemical cleaning method. In the second stage, stone blocks were used to investigate the mechanisms of salt induced decay after chemical cleaning. This work covered the laboratory testing of samples, the cyclical weathering of samples and the field testing of samples. The final stage involved the statistical analysis and reporting of the results from the previous stage.

3.2 Stone characterisation

3.2.1 Petrological analysis

Petrological analysis involved the preparation of thin sections of stone on glass microscope slides. Thin sections were used to observe the alteration or weathering of the grains and minerals as well as the stone colour and porosity.

The stone was impregnated with a blue coloured resin prior to slicing. This has the advantage of highliting pore space. Thin sections were examined under an optical, polarised light microscope to reveal the stone's mineralogy and structure. Petrological analysis of stone samples in this way will give details of the type and amount of mineral grains and cement in the stone, grain size, shape and sorting, decay or alteration of minerals, the depth and thickness of the soiling layer and an estimate of porosity.

The mineralogy of the sandstones was determined by optical microscopy. The composition of the stone forming minerals is shown in Table 3.1. The petrographic data for each stone are shown in chapter 4 (Table 4.1).

Table 3.1 Composition and harness index of stone forming minerals.

Mineral name	**Composition**	**Hardness index**
Quartz	SiO_2	7
Microcline feldspar	$(Na)K[AlSi_3O_8]$	6-6.5
Plagioclase feldspar	$Na[AlSi_3O_8]$	6-6.5
Orthoclase feldspar	$K[AlSi_3O_8]$	6
Muscovite mica	$K_2Al_4[Si_6Al_2O_{20}](OH,F)_4$	2-2.5
Biotite mica	$K_2(Mg,Fe)_5(AlSi_2)OH(OH,F)_2$	1.5-3
Iron oxide/hydroxide	$Fe_2O_3/FeO.OH$	5.5-6
Kaolinite	$Al_4[Si_4O_{10}](OH)_8$	2-2.5
Vermiculite	$(Mg,Fe,Al)_6[Al,Si)_8O_{20}](OH).8H_2O$	2-2.5
Illite	$K_2Al_4[Si_7AlO_{20}](OH)_4$	2-2.5

3.2.2 *Chemical analysis of sandstones*

Chemical analysis of the Locharbriggs (Young, 1998) and Crossland Hill (Johnsons, Wellfield Quarries) sandstones was made by X-ray fluorescence spectroscopy (Table 3.2). The rock sample was crushed to a fine powder and dried to 105°C to remove any adsorbed water from the sample. Two pellets were prepared for analysis. One was made by compressing a sample of the rock powder mixed with an organic glue. This sample was used to determine the sodium (Na) content of the sample. A second pellet was prepared from powder which had been heated to 900°C to remove water, CO_2 and SO_3 from the sample. The weight loss at 900°C was measured and was given in the final analysis as LOI (loss on ignition). The powder was mixed with a flux material and then melted and moulded into a flat glass pellet. This pellet was used to measure all major elements: silicon (Si), titanium (Ti), aluminium (Al), iron (Fe), manganese (Mn), magnesium (Mg), calcium (Ca), potassium (K) and phosphorus (P).

Table 3.2 Chemical composition of sandstones as determined by X-ray fluorescence

Chemical properties	Locharbriggs[1], %	Crossland Hill[2], %
Silica	91.20	85.79
Aluminium oxide	2.80	6.88
Ferric oxide	0.73	1.73
Calcium carbonate	0.19	0.58
Alkalis	1.86	1.67
Loss on ignition	0.47	2.02

[1] Young (1998); [2] Johnsons, Wellfield Quarries

3.2.3 Analysis of clay mineralogy of sandstone by X-ray powder diffraction

Sandstones were fragmented and ground with deionised water in a mortar and pestle to disaggregate the stone. The mixture was left to settle for 3-5 minutes and then decanted. This process (Young, 1998) was repeated until the water after settling was clear, the clays having then been removed to the decanted water. The liquid was centrifuge for 10 minutes at 6000 rev/min to separate the fines out. The fines were collected into a centrifuge tube and shaken up to disperse the clay particles. This mixture was centrifuge for 3 minutes at 800 rev/min. The clay fraction (<2 μm) remained in suspension as a cloudy liquid. A glass pipette was used to transfer sample of the clay fraction onto a glass slide which, when dried could be used for X-ray diffraction identification of the clay minerals. The X-ray used were Co K-alpha at 40mA and 40kV. Samples were scanned from 5 to 40 degrees. The output was analogue and peaks were identified by visual comparison to known standard diffraction patterns obtained from JCPDS files (Joint Committee on Powder Diffraction Standards). The data are shown in chapter 4 (Table 4.2).

3.3 Chemical cleaning of sandstones

3.3.1 Application

An acid-based cleaning method widely used on sandstone in the past in Scotland was selected to represent the cleaning treatment in the investigation (Section 1.2.2). All cleaning products commercial names will remain in confidence.

Application of rinsed water under high pressure was extremely important so that all solubilised staining elements are driven from the pores of the masonry. High pressure pumping equipment provided the minimum 600 psi (4.13 Mpa) at 12 litres per minute. Alkaline degreaser was applied using a soft bristled nylon brush and the hydrofluoric acid cleaning solution with a densely filled masonry washing brush. All chemicals were used with adequate ventilation and required use of rubber gloves, eye protection, face shield, rubber rain suit and other personal protective equipment so as to avoid splash to skin and eyes. Also approved respirators for use with acids.

The stone surface was pre-wetted with deionised water. Afterwards, a thin coating of alkaline degreaser, sodium hydroxide, 20% w/w (1:3 diluted) was applied using a brush. After 30 minutes, the samples were rinsed with deionised water under high pressure (600 psi) and then the cleaning solution, hydrofluoric acid, 6% w/w (1:3 diluted), was applied using a brush. After 5 minutes low pressure rinsing was used to remove the initial acid residue. The treated area was then rinsed thoroughly using high pressure spray (4.13 Mpa). The results from the composition of chemical cleaning agents are shown in chapter 4 (Table 4.3).

Testing of stone pH was conducted before and after chemical cleaning to ensure that neutralisation of cleaning agents has taken place. pH test strips which can be moistened with liquid taken from the stone sample were used and multiple readings were taken to improve accuracy.

3.4 Testing methods

3.4.1 Depth profiling

Depth profiling was the technique selected to monitor the presence and distribution of potentially damaging soluble salts in the stone before and after undertaking the different investigation stages of the work. This technique not only will offer information about the fate of retained chemicals from the cleaning process but also about other soluble salts presence within the stone matrix or derived from the environment to which they were exposed.

To obtain a depth profile in sandstones, useful sampling depths have typically been 0.5 to 2 mm intervals to depths of up to 20 mm from the stone face. The soluble salts are then extracted into distilled water from rock powder and analysed by ion chromatography, atomic absorption and ion selective electrode.

Two methods can be selected for obtaining the rock powder for analysis and both are equally successful (MacDonald, 1993). The first method, and the one chosen in this project, involves drilling in measured stages to a depth of 2 cm using a flat tipped tungsten carbide 10 mm diameter drill. At each depth the drill is raised and the rock powder collected. The process is repeated at a number of different points over the sandstone surface until enough sample (0.5-1 g) had been collected. This process ensured a representative sampling over the area of interest. Successive drillings are repeated until the total required depth is reached. The second method involves dry sawing the stone in successive slices of the required sampling depth. In both cases, a powder is produced and not further milled is required as this could increase the extraction of ions from the minerals.

Typically a powder sample of 0.5 g is accurately weighed and then a volume (50 ml) of distilled water is added. The plastic container is then shaken for 1 hour and left to equilibrate for 30 minutes before filtering the sample using a vacuum filter system to remove particulates.

3.4.2 Leaching extraction

The modified method was adopted from a desalination study commonly used in conservation (Costa Pessoa, 1996). The experimental studies on the leaching of soluble residues with time were carried out at room temperature, in the presence of deionised water and in a closed system with a partial pressure of CO_2 of 1 atmosphere. This method provided information on the dissolution trends of several soluble ions before and after the chemical cleaning process (Chapter 5) and before and after field exposure (Chapter 8).

Samples were immersed for one month in 3000 mL of deionised water in closed plastic containers, and salt removal was monitored for one month at times 0, 5, 15 and 30 days by sampling aliquots of 30 ml. Mechanical stirring was applied during all the time. Two analysis were undertaken for each ion and the results were normalised by dividing them by a factor m/V, where m is the weight in grams of the stone sample and V the volume of immersion water in litres.

3.4.3 Chemical analysis of salts (IC, AA and Fluoride selective electrode)

All the experiments with ion chromatography used a Dionex model 4500 Ion Chromatograph with an autosampler. Data analysis was provided using a Spectra Physics model SP4270 integrator. A Dionex AS4A anion separating column and AG4A guard column (both 4 mm ID) were used together with an ASRS-1 anion supressor operating in recycle mode. The eluent used was a mix of 1.7 mM sodium carbonate / 1.8 mM sodium hydrogen carbonate solution pumped through the columns at 2.0 mL/min. Samples were placed into 5 mL Dionex sample vials with filter caps and were injected onto the columns using a 50 µl plastic injection loop. The resulting anion peak areas were calculated by the integrator.

Atomic absorption spectrophotometry was carried out on a Perking Elmer model 3100 AA spectrophotometer using an air-acetylene, fuel-lean flame. The wavelengths were set at 766.5, 589 and 285.2 nm for the corresponding maximum high absorptions for K, Na and Mg. Readings were adjusted to zero by aspiring distilled water prior to each standard solution. Standards solutions containing: 0.5, 1.0 and 2.0 mg/L for potassium (K); 0.2, 0.5 and 1.0 mg/L for sodium (Na) and 0.1, 0.3 and 0.5 mg/L for magnesium (Mg) were prepared by successive dilution of the corresponding stock (1000 mg/L). Each working standard solution was measured 2 times in ascending order and an average taken for each concentration.

Optimisation procedures were standardised (lamp energy, burner head and nebuliser) and kept constant for all analysis.

All standards and samples were pipetted an accurate quantity (10 mL) of caesium chloride and lanthanum oxide (10 000 mg/L) into a 100 mL standard flask to reduce interferences. Lanthanum oxide was added to reduce the effect of silicon and aluminium on magnesium and caesium chloride to control the partial ionisation of potassium and sodium in the flame.

Ion-selective electrode (Model 94-4099 Russel) was the method selected for the determination of fluoride. A series of standards solutions of 0.1, 0.5, 1.0 and 2.0 mg/L fluoride were prepared from the standard solution Russel 0.1 M sodium fluoride. Analysis of standards and samples involved the same following procedure. The solution to be determined (25 mL aliquots) was pipetted into a 100 mL polypropylene plastic beaker together with a PTFE magnetic bead. The electrode was soaked in deionised water prior to use. Emf readings were then recorded every minute until consecutive readings agreed to within 0.1 mV. This was considered to be the equilibrium emf and was recorded. Duplicate aliquots were measured until two measurements agreed to within +/- 0.5 mV.

All reagents used for the preparation of the eluent in the ion chromatography, standards solutions for IC, AA and ion selective electrode were grade and deionised water (18 MΩ) was used in all cases.

3.4.4 Colour testing

Quantification of colour is important to evaluate the action of the cleaning agents on the original colour of the stone surface and also to monitor the changes during its weathering.

The colour analysis of the stone surfaces was done using a chroma meter (Minolta colour meter CR-200). This is a battery powered, hand held device for measuring reflected-light colour. It works by projecting a bright beam of light (pulsed xenon arc lamp) onto the surface selected. The reflected light is analysed in a series of high sensitive silicon photocells. The data are obtained as a colour scale classified into three components: L (brightness) measures the lightness level on a scale of 0% (black) to 100% (white); a (green to red) and b (blue to yellow) are chromaticity co-ordinates, 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). Colour testing was always carried out on dry surfaces as wet stone is significantly different in colour.

3.4.5 *Stone porosity*

The PoroSizer 9320 is a 30,000 psi (207 Mpa) mercury porosimeter covering the pore diameter range from approximately 360 to 0.006 µm. The unit has two built-in low pressure ports and one high pressure chamber. Data collection, data reduction and data display were processed by the control module (Photo 3.1).

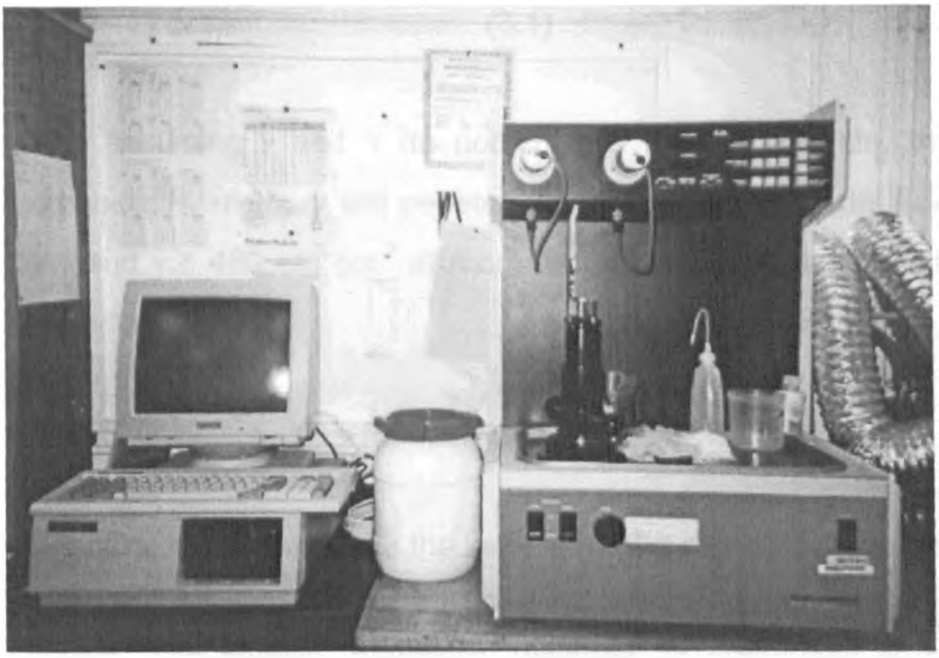


Photo 3.1 Mercury porosimeter used in the experimental work.

The PoreSizer measures the volume distribution of pores in sandstone by mercury intrusion or extrusion. Mercury has a high surface tension and is non-wetting to all materials with exception of a few noble metals. These properties cause a mercury surface in contact with a solid to assume the minimum surface area and largest radius of curvature possible at a given pressure. An increase in pressure on the mercury shifts the balance between surface tension and surface area causing the radius of curvature of the mercury contacting the solid to become smaller. When the radius is equal to that of a pore entrance, mercury fills the volume within the pore.

The IUPAC classifies pores into three classes:

- micropores, d < 20 nm
- mesopores, 20 nm < d < 50 nm
- macropores, d > 50 nm

Mercury porosimetry is only used to investigate meso and macroporosity as the pressure required to penetrate a pore r = 18 nm is 60000 psi (414 MPa) which is the maximum pressure reached by the actual porosimeters.

Pressure (P) and superficial tension (γ) are related to the contact angle (θ) formed by the mercury and the capillary walls (r) as exposed in Washburn equation 3.1:

$$P * r = -2\gamma \cos\theta \qquad (3.1)$$

Assuming γ and θ do not change then $P * r =$ cte, this means that increasing P, mercury will penetrate pores of smaller radii. For mercury, θ = 140° and γ = 480 $erg*cm^{-2}$ at room temperature and therefore the expression above ends up as:

$$r = 106.7/P \qquad (P = Mpa; r = \mu m)$$

The method requires the vacuum of the sample prior to the application of pressure. This increasing pressure will force the mercury to enter the porosity network. The sample, previously weighed, is introduced in a penetrometer which is formed by a sample container connected to a calibrated tube and an electrode.

The graphical representation of volume of mercury versus P or r (intrusion curve) is finished once the system has reached the maximum pressure fixed for the experiment, then the reversal process starts (extrusion curve). In general, both curves do not correspond to each other giving origin to the phenomena known as histeresis. There are different theories to explain this effect but in general it can be assumed that some mercury will left in the stone (Rey Bueno, 1996).

The information provided by the distribution of mercury as a function of the radii is limited, especially when coming to explain chemical activity of the sample, for example its decay under certain conditions. In this case, it is far more useful to work with superficial areas. Samples of porosity larger than 50 nm have a low chemical activity because of the small superficial area. On the other hand, samples with porosity less than 20 nm have a larger superficial area and therefore more chemically active. From the intrusion curve, it is possible to measure the accumulated area from all pores in a determined pressure range, independently of the geometry of the pore. The pore size distribution was calculated using the cylindrical model (Cook and Hover, 1993).

3.4.6 Scanning electron microscopy

This technique enables examination of the surface of the stone at a very small scale and across areas of few microns.

The scanning electron microscope utilises a focused beam of high energy electrons (usually 20 keV) that systematically scans across the surface of the specimen. This interaction will produce low energy secondary electrons which can be collected into a detection system. The electron signal is then converted into an electronic signal which is portrayed on a cathode ray tube. The result is an image of great resolution at very low and very high magnifications (Postek *et al.,* 1980).

Typically, small samples (1-2 cm diameter) were mounted on a aluminium stub used to support the specimen and attach it to the microscope stage. Stones do not naturally conduct electricity and cause problems in the SEM unless they can be made conductive. Coating specimens with a thin layer of a conductive material (Au/Pd) helped to overcome these problems.

The electron microscope used in this project was a Cambridge Instruments Scanning Electron Microscope model S90B with electron disperse analysis (EDX) facility attached to it and therefore it was also possible to analyse the chemical elements which are present in a chosen area or mineral grain.

Elemental analysis of a sample was obtained by collecting the characteristic x-rays generated as the electron beam scanned the sample. These x-rays can be analysed using an energy sensitive Si (Li) detector in an energy dispersive system. The EDX system was used to obtain rapid analysis of elements above atomic number (Z) = 11 (sodium).

The applications of SEM in this project can be divided into two groups:

1. Study of the stone material: identification of minerals and its physical state; qualitative study of new formation products; analysis of biodecay caused by algae, fungi and lichens; stonecleaning and artificial or field exposure effects.
2. Study of soluble salts: growing conditions, location in the stone minerals and composition.

For all samples, the operating conditions were kept constant: beam voltage (15 keV), the area being analysed and the number of counts for the chemical analysis (3000). The ions selected for the elemental map analysis and their colour on the photomicrographs were: sodium (green); magnesium (magenta); sulphur (cyan); chlorine (yellow); potassium (red); calcium (blue) and iron (orange).

3.5 Artificial weathering methodology

3.5.1 Partial immersion in salt solutions

Sandstone cores (40 mm height by 20 mm diameter) were partially immersed in three solutions of 0.1 M NaCl, 0.1 M Na_2SO_4 and artificial seawater (0.3 M and 0.01 M Na_2SO_4) for four months and compared to a control sample immersed in deionised water. This method described by Sperling and Cooke (1985) allows capillary rise, concentration by evaporation and crystallisation of the salt in a narrow zone of the sample. It also simulates the situation in which lower walls of buildings are affected by capillary rise and therefore exposed to salt weathering.

The experiments were carried out at room temperature (20°C) and each core was immersed in an independent closed plastic container and in all cases, the immersion in salt solutions was at a constant depth of 1 mm. This situation intended to simulate a single damage process due solely to crystallisation pressure. The changes in porosity and pore size distribution were evaluated by means of mercury porosimetry. The compressive strength measurement was performed to determine direct compression strength. The number of specimens used were two per sample as recommended by the standard test method for compressive strength of natural building stones (Brown, 1981). The tensile strength was calculated by dividing the maximum load applied to the specimen by the original cross-sectional area (La Iglesia *et al.*, 1996).

3.5.2 Cycling weathering studies

Simulation of wet/dry cycles in Section 7.1 was undertaken in a BR590H cabinet fitted with temperature and humidity control (Photo 3.2). A two set point cycling control system and cooling system were available. Two setpoint cabinets have a 24 hour cycle timer, which switches the cabinet between the two temperature and humidity setpoints. Humidification was achieved by introducing water vapour into the treatment chamber from a vapour phase generator. The vapour phase generator operates by heating distilled water and the rate of humidification depends upon the amount of heating. A squirrel digital data/logger was set up for recording air temperature and relative humidity at intervals of 90 minutes. At least 100 measurements were taken during the recording interval, these were averaged and stored at the end of each recording interval.

Photo 3.2 BR590H cabinet used for the simulation of temperature and humidity cycles.

The experiment was set up to evaluate the effects of two salts on Locharbriggs and Crossland Hill sandstone blocks (80 x 80 x 40 mm) under the same artificial weathering conditions: single immersion in 0.4 M Na_2SO_4 (hydratable salt) and in 0.6 M NaCl (non-hydratable salt) followed by application of daily wet/dry cycles based on field data from a representative Scottish environment (Metereological Office).

The cycle used in the BR590H cabinet represented a typical humid summer conditions, characterised by a daily variation of temperature at the stone surface and high but variable relative humidity. The daily temperature range was between 5°C and 35°C and the humidity range between 70 and 90 per cent. Within the RH/T cycles, dew point was reached where condensation of water vapour onto the stone surfaces in the chambers occurred.

Simulation of water spray at two different pH (Section 7.3) was undertaken in a MPC/PB5 spray chamber. This chamber permitted the control of spray emission and the introduction of a drying period under a controlled drying temperature (Delgado, 1989). For the water spray at pH 4, a solution of H_2SO_4, 1% concentration was used. Each cycle lasted for 24 hours with 12 hours of water spray and 12 hours of drying at a temperature of 40°C. For the control test, water spray at equilibrated pH 5.6 was used.

For this study, three sandstone samples of each type were selected (35 x 35 x 35 mm), one sample was only water washed and used as control while the other two were chemical cleaned. The samples (exposed to a water spray system of pH 4 and pH 5.6) were removed from the chamber once (loss 1 after 12 cycles) during the whole period of exposure and at the end (loss 2 after further 28 cycles) in order to monitor any weight change. The reported total weight loss is the average for two identical samples after a period of 40 cycles.

Simulation of exposure to SO_2 (Section 7.2) was carried out in the atmospheric corrosion chamber (VSK300). It had the main advantage of the high accuracy in the control and regulation of temperature, gas flow, relative humidity and concentration of SO_2. The main features are the chamber where samples are exposed together with an internal unit attached to it for controlling the gas flow.

The working limits for this chamber are (10%, 98%) relative humidity and (+10°C, +90°C) temperature. For the SO_2 gas, the limits of concentration are between 0.2-20 mg/L (pre-diluted in N_2, 1%); the air flow can be adjusted between 0.5-1.5 m^3/h.

The gas control unit is fitted with a vacuum pump. The difference in pressure between the internal unit and the atmospheric pressure is controlled by a pressure regulator and equilibrium is established.

$$ppm = \frac{60Vs}{Va}$$

$$ppm = \frac{60Vs}{Va} = \frac{60Vp\%gas}{100Va}$$

Va = output air flow entering the gas unit (m^3/h)
Vp = gas flow controlled by the internal unit (mL/min)
Vs = SO_2 concentration in the gas flow, Vp (mL/min)

$$Vp = \frac{100ppmVa}{60\%SO_2}$$

Therefore, for a 10 ppm (mg/L) SO_2 gas exposure experiment, 1 m^3/h air flow and 1%SO_2 in N_2, the gas flow, Vp would be:

$$Vp = \frac{100 \times 10 \times 1}{60 \times 1} = 16mL / min$$

Five samples of each sandstone type were used (35 x 35 x 35 mm), one sample was only water washed and used as control while the other four were chemical cleaned. These samples were cut into two so one half was exposed to SO_2 gas with a constant flow of 10 mg/L at 25°C and 80% relative humidity for 12 days and the other half was used as a reference control. These conditions were similar to the ones used in sulphation studies by Mangio *et al.,* (1991). The exposed samples were removed from the chamber once during the whole period of exposure in order to monitor any weight change. Analysis of soluble anions (chloride, nitrate and sulphate) was carried out by using the depth profiling technique.

3.6 Field studies

The possibility of environmental/climatic influence on the action of salts in cleaned sandstone (dry/wet cycles, salt crystallisation and salt migration) was investigated by exposing stone samples of Locharbriggs and Crossland Hill to four different locations around Scotland (Banff, rural-coastal; Dunkeld, rural-inland; Aberdeen, urban-coastal and Glasgow, urban-inland).

The advantage of field studies is that the samples are exposed to realistic levels of the environmental variables acting in combination. Some disadvantages are that there are only a limited number of suitable sites available and within this set there may be a very small range of variation of the environmental variables of interest. Another disadvantage is that the environmental variables are not controlled, but instead must be monitored at each site. Also it might take a long period of time to obtain meaningful results.

The test stands were specially designed for the study (Photo 3.3a-b) and support four samples from each sandstone type (one control and three chemically cleaned). All the samples are exposed as prisms of certain dimensions (80 x 80 x 40 mm).

Samples were exposed for 24 months and the changes in porosity and pore size distribution, chemical distribution of soluble ions, colour and superficial changes were evaluated and compared to the initial values before exposure.

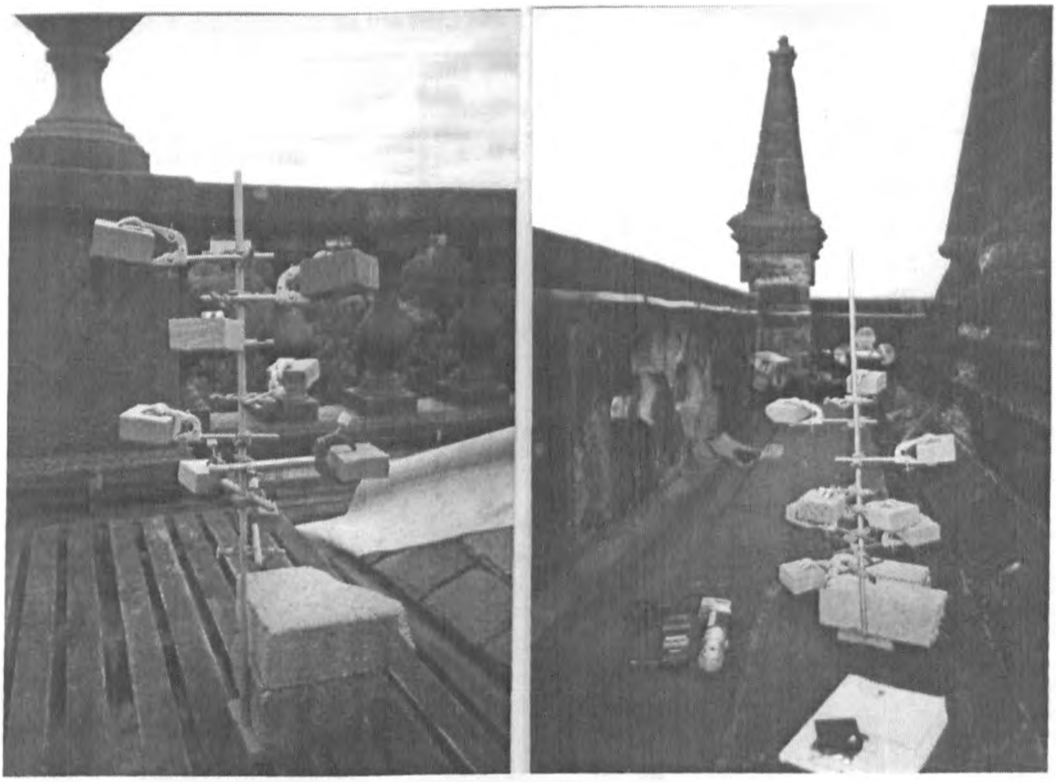


Photo 3.3 Examples of test stands used for the field studies in Dunkeld (left) and Glasgow (right).

3.7 Climatic and pollution data

Air pollution data (SO_2 and NO_2 levels) were obtained from the City of Aberdeen Environmental Development Division and relate to a monitoring site at Union St in Aberdeen, within 1 km of the test stand. The mean air pollution levels for the period between 94-96 were of 127.2 µg/m^3 for NO_2 and 20 µg/m^3 for SO_2. Both within the EC limit set at 200 µg/m^3 and 100 µg/m^3 respectively.

Climatic data (Table 3.3) were obtained from the Metereological Office at the four stations (Figure 3.1) where the field site studies were carried out (Glasgow-Abbotsinch, Aberdeen-Dyce, Dunkeld-Faskally and Banff-Banff golf course). In terms of climate, the following parameters were considered in the studies: precipitation, temperature, wind exposure, sunshine.

Table 3.3 Climatic data for all the field sites.

Data	Site and Mean values 96-97			
	Glasgow	Aberdeen	Banff	Dunkeld
Total yearly rainfall (mm)	930.5	895.5	367	434
Total yearly sunshine (h)	1428.7	1420.8	1400	1450
Daily mean temperature (°C)	11.1	8.7	6.9	6.5
Gale wind (days)	6	4	2.5	0.5
Snow (days)	34	33	18	16

All data from Metereological Office

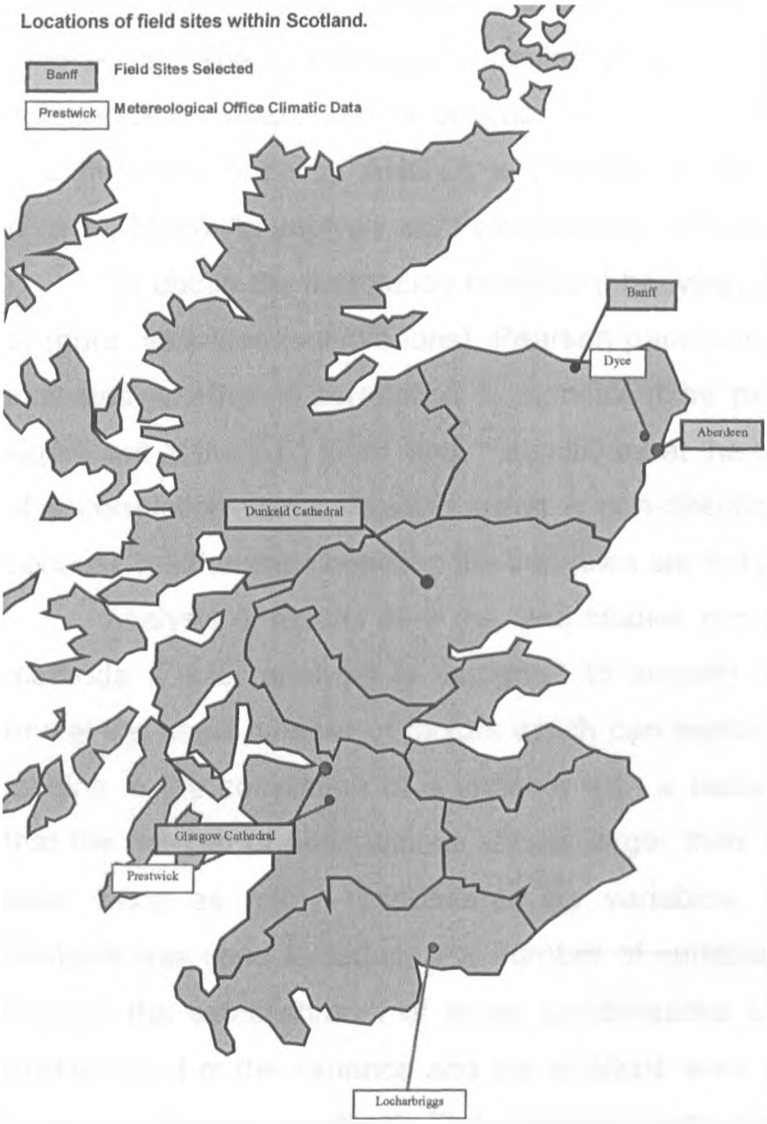


Figure 3.1 Location of field exposure sites and meteorological stations (Scotland map)

3.8 Statistical analysis

Statistical analysis of the results from the depth profiling and leaching experiments involved comparison of the mean values for the different soluble ions. The methods selected were one-way ANOVA and correlation analysis.

One-way ANOVA allowed comparison of the mean values among the ion concentrations (Miller and Miller, 1993). The dependent variables were identified as chloride, nitrate, sulphate, fluoride, sodium, potassium and magnesium. The independent variables were: location, depth and time. Each independent variable was a between-subject variable (independent samples) and therefore one-way ANOVA is the best method of analysis of variance (Foster, 1998). All analysis were executed by SPSS statistical package.

To obtain the correlation coefficient between all possible pairing of three or more variables (soluble ions), Pearson parametric test was selected. SPSS indicates whether a correlation is significant by printing asterisks: *indicates significant at the 0.05 level, and ** significant at the 0.01 level. The significance of a correlation was calculated using a non-directional (two-tailed) probability because relationships between the variables are not predicted.

Analysis of results after the field studies required additional multivariate methods. Factor analysis is designed to simplify the correlation matrix and reveal the small number of factors which can explain the correlations. A factor loading is the correlation of a variable with a factor. Foster (1998) considers that the number of observations should larger than 10, and there should be at least twice as many respondents as variables. The principal component analysis was used to reduce the number of variables included in the data set through the establishment of linear combinations between the variables that explain most of the variance and the analysis were run with rotation of factors using the Varimax method. The approach was similar to the one used by Moropoulou *et al.,* (1995). A data matrix is formed with the values of the chemical analysis of the soluble salts, expressed as percentage change with exposure. Then, three more variables are added to represent the climatic parameters (rainfall, temperature and gale wind). The graphical representation of the principal components shows the contribution of each variable to each factor and their correlation. Finally, discriminant analysis on the data set is carried out in order to classify observations as a function of location. The variables used are the same as above and the classification factor is the geographical location: 1 (Glasgow), 2 (Aberdeen), 3 (Banff) and 4 (Dunkeld). This procedure determines the linear combination of predictor variables that best classifies cases into one of several known groups. It can use this solution to classify cases whose group is unknown.

4 SANDSTONE CHARACTERISATION AND CHEMICAL REACTIONS BETWEEN MINERALS AND CLEANING AGENTS

4.1 Sandstones Characterisation

Two sandstone types were used in the studies, Locharbriggs sandstone and Crossland Hill sandstone (Table 4.1). Locharbriggs is a red, medium to coarse grained Scottish sandstone of Permian age. The mineralogy of Locharbriggs as observed by a polarising microscope (Photo 4.1a) is: quartz, 91%; microcline feldspar, 2%; plagioclase feldspar, 2%; orthoclase feldspar, 3%; muscovite mica, 1%. The cements are iron oxides, silica overgrowths and traces of clays. Despite the deep red coloration, the iron oxide cement is only present as a thin coating on the surface of the detrital grains and cementation mainly originates from deposition of siliceous cements. The grains are well sorted with high sphericity. The porosity, measured by mercury porosimetry, is high at 22.4% with a saturation coefficient of 0.64. Porosity is intergranular rather than within grains however the feldspar appears porous due to dissolution. There is some alignment of grains to form fine banding. There is some evidence of compaction and pressure solution with overgrowths on the quartz and some feldspar grains (Young, 1998).

Crossland Hill sandstone is a quartz arenite, light brown-buff coloured, fine to medium grained stone of Carboniferous age. The mineralogy as observed by a cross polarising microscope (Photo 4.1b) is: quartz, 77%; microcline feldspar, trace; plagioclase feldspar, 2%; orthoclase feldspar, 10%; muscovite mica, 3%; biotite mica, 3%; iron oxide/hydroxide, 5%. Clay occurs in rare intergranular pockets. There is no carbonate. Monazite occurs as an accessory phase and iron oxide is very minor as small irregular grains. It is very well cemented by quartz overgrowth and pressure solution and within domains of the rock intergranular porosity is effectively zero. The grains are well sorted with subrounded to subangular grains. The porosity is very low at 9% with a saturation coefficient of 0.62. This sample is also likely to be a durable building stone with a low permeability to water (Leary, 1992).

Table 4.1 Summary of some properties of the sandstones selected.

Sandstone	Porosity %	Specific gravity, g/cc	Mean grain diameter, μm	Saturation coefficient	Colour
Locharbriggs	22.4	2.17	350	0.64	Red
Crossland Hill	9	2.56	300	0.62	Light Brown

4.2 Petrographic analysis

Blue-dyed resin impregnated thin sections were prepared for each sample (Photo 4.1a-b), and examined using standard transmitted polarising light optical microscopy. The data are shown in Table 4.2.

Table 4.2 Petrographic data on sandstones used in experiments.

Sandstone	**Type**	**Minerals, %**						
		Quartz	**Microcline Feldspar**	**Plagioclase Feldspar**	**Orthoclase Feldspar**	**Muscovite Mica**	**Biotite Mica**	**Iron oxide/ hydroxide**
Locharbriggs	Quartz arenite	91	2	2	3	1	0	0.73
Crossland	Quartz arenite	77	trace	2	10	3	3	5

Sandstone	**Grains**			
	Max. size, μm	**Modal size, μm**	**Roundness**	**Sorting**
Locharbriggs	750	400	very good	very good
Crossland Hill	350	300	moderate	good

4.3 Analysis of clay mineralogy of sandstone by X-ray diffraction

The data from the analysis of clay minerals identified in the two sandstones selected for this study are shown in Table 4.3.

Table 4.3 Clay minerals identified in sandstone by X-ray powder diffraction and optical microscopy (Young, 1998).

Sandstone	**Clay type**	**Amount**	***Approx. %**
Locharbriggs	illite	major	2
	interstratified illite-smectite	minor	< 1
Crossland	kaolinite	trace	< 1

**using microscopic data*

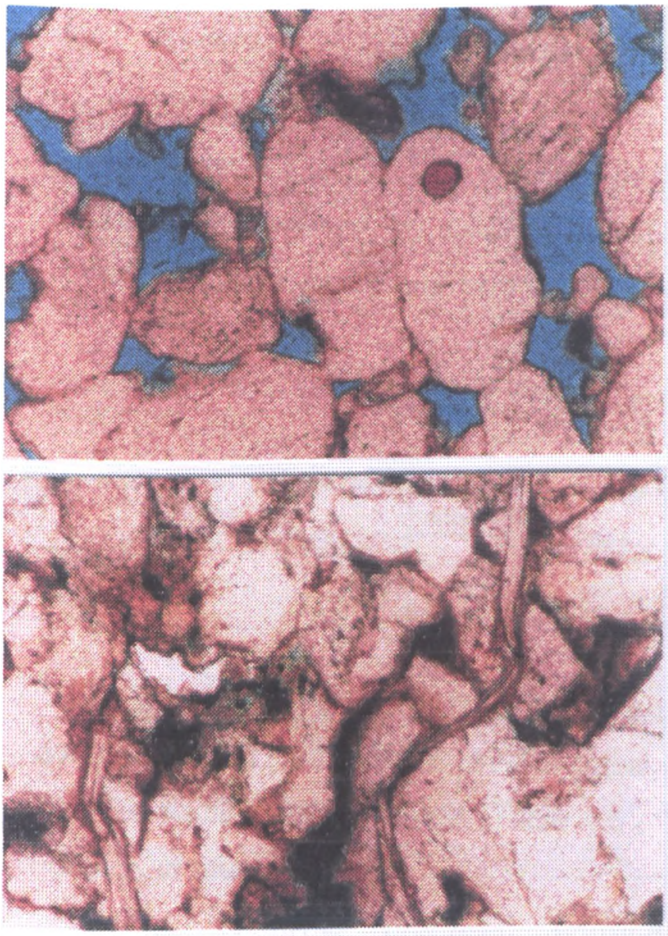


Photo 4.1a-b Images of Locharbriggs (top) and Crossland Hill (bottom) sandstones by optical microscopy.

4.4 Reactions between minerals and cleaning agents

Diluted samples of the commercial cleaning agents, caustic gel and acid liquid, were analysed for sodium by atomic absorption and for the anions fluoride, sulphate and phosphate by ion chromatography (Table 4.4).

Table 4.4 Composition of chemical cleaning agents used on sandstone samples for all experimental work.

Alkaline treatment			**Acid treatment**		
Material type	Composition	Working conc. (%w/w)	Material type	Composition	Working conc. (%w/w)
Caustic gel in water solution	NaOH	6	Acid liquid in water solution	HF H_3PO_4 H_2SO_4	2 1.5 0.1

The dissolution reactions expected between minerals and cleaning agents (HF and NaOH) were used to calculate the standard free energy change and the equilibrium constants (Table 4.5). These values were used to predict reaction products.

The following proposed equilibrium reactions represented the composition of the sandstones in this project (potash feldspar, mica and kaolinite).

Equilibrium 1: K-feldspar (Holdren Speyer, 1985).

$KAlSi_3O_8 + 22HF \xleftrightarrow{H_2O} 3H_2SiF_6 + AlF_3 + KF + 8\,H_2O$

Equilibrium 2: mica (Wilson, 1987).

$2\,KAl_3Si_3O_{10}(OH)_2 + 2HF \xleftrightarrow{H_2O} 3\,Al_2Si_2O_5(OH)_4 + 2KF + H_2O$

Equilibrium 3: kaolinite (Brosset, 1943).

$Al_2Si_2O_5(OH)_4 + 18HF \xleftrightarrow{H_2O} 2H_2SiF_6 + 2\,AlF_3 + 9\,H_2O$

Equilibrium 4: K-feldspar hydrolysis (Hay, 1963).

$KAlSi_3O_8 + 22\,H_2O \xleftrightarrow{H_2O} 4K^+ + 4OH^- + 8\,H_4SiO_4 + Al_4[Si_4O_{10}](OH)_8$

The relation of free energy change to equilibrium constant for the special case in which all substances are present at unit activity, is expressed as:

$\Delta G^0 = -RT \ln Ka$ (Atkins, 1986)

The standard free energy change for these reactions was calculated from the equilibrium reactions by subtracting the sum of the ΔG^0 values for the reactants from the sum of ΔG^0 values for the products (CRC, 1996) (Table 4.5).

Table 4.5 Free energy change (ΔG^0) and equilibrium constant (K) values were calculated at 1at pressure and 25°C.

Reaction equilibrium	**ΔG^0 kJ/mol**	**Equilibrium constant, K (25°C)**
Equilibrium 1	-276.3	10^{48}
Equilibrium 2	-954.4	10^{167}
Equilibrium 3	-396.9	10^{70}
Equilibrium 4	-10807.7	10^{1893}

The negative ΔG^0 and the large exponent in K mean that the reactions for feldspars mica and kaolinite are displaced towards the right.

The dissolution of feldspar at acidic pH (Equilibrium 1) resulted in the preferential release of aluminium and potassium, these in combination with fluoride can deposit as salts in the pore network. At high pH, silicate hydrolysis (Equilibrium 4) lead to the production of hydroxy groups which in combination with other cations in solution can also lead to precipitation of salts in the pore network.

Some experimental work on the dissolution of minerals has shown that for feldspars dissolution processes will be the same at pH1 and pH6 (Nahon, 1991). However, dissolution reactions are faster and the relative elimination of cations is better developed at pH6.

The dissolution of mica at acidic pH (Equilibrium 2) would indicate the release of potassium cations into solution or its precipitation as KF.

Kaolinite will react with HF to form silicon and aluminium fluorides (Equilibrium 3). As aluminium dissolves, it combines with the available fluorine and the reduction on HF concentration can lead to the precipitation of $Si(OH)_4$, a hydrated colloid that reduces the stone porosity (Labrid, 1975).

5 EVALUATION OF CHEMICAL CLEANING EFFECTS ON SANDSTONE

5.1 Porosity and Pore size distribution

The porosity and pore size distribution for both sandstones, untreated and chemically cleaned, indicated a decrease (- 4.18%) in the overall porosity after cleaning for the Locharbriggs type and an increase (2.78%) for the Crossland type (Table 5.1).

Table 5.1 Porosities of sandstones measured by mercury porosimetry.

Sandstone	Treatment	Mean porosity, %	sd	Δporosity, %
Locharbriggs	None	22.41	0.12	-4.18
	Chemically cleaned	18.23	0.14	
Crossland	None	9.75	0.30	2.78
	Chemically cleaned	12.53	0.42	

Raw data in Appendix 5.1

These variations in overall porosity for both sandstones after chemical cleaning can be interpreted, in the case of the Locharbriggs stone, as a deposition of salts after application of HF probably from reaction with the clays (Section 4.4). On the other hand, the increase in porosity for the Crossland Hill stone would indicate the removal of the soiling layer with the consequent opening of porosity.

During the acid cleaning treatment, the sandstone surface was in contact with 2% HF and 1.5% H_2SO_4 for 5 minutes (see chapter 3). During this time the acid would be exposed to sufficient aluminium-bearing minerals so that silica precipitation begins to occur (Equilibrium 5.1) and normally a distribution of reaction products (silicon and aluminium fluorides) will coexist (Brosset, 1943). Ashurst (1994) also reported the presence of white insoluble residues on the surface of sandstones after contact with HF. These residues were the re-deposition product of dissolved siliceous mineral. This would explain the reduction in porosity for Locharbriggs after chemical cleaning.

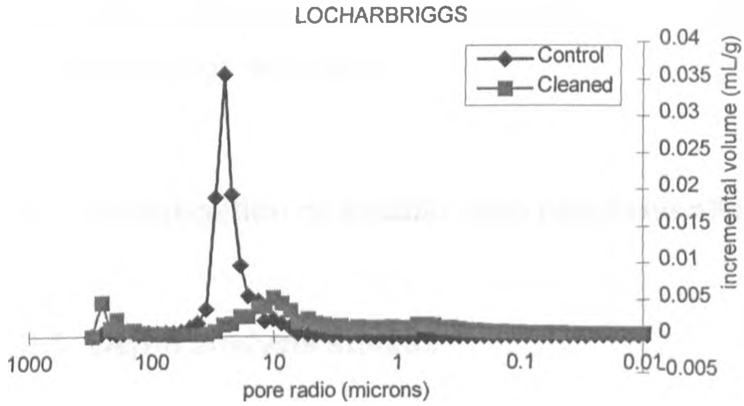
$$Al_2Si_2O_5(OH)_4 + 18HF \xleftrightarrow{H_2O} 2H_2SiF_6 + 2\,AlF_3 + 9\,H_2O \text{ (Equilibrium 5.1)}$$

In both cases, the cleaning treatment had an important effect in the overall porosity, either to close or to open up pore space. The type of reactions expected between minerals and cleaning agents (HF and NaOH) are better understood by looking at the fundamental mechanisms of silicate dissolution (Section 1.4 and Section 4.4).

Examination of the pore size distribution shows which pore size region is more affected after the chemical cleaning.

Figure 5.1a-b shows the porosity distribution before and after chemical cleaning for both sandstones.

(A)



(B)

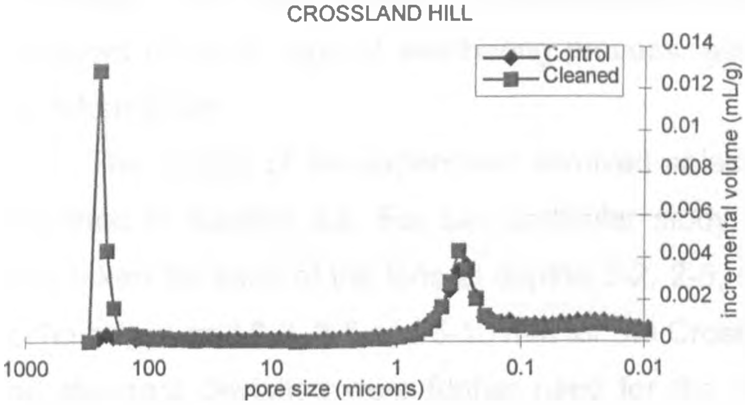


Figure 5.1a-b Porosity distribution of Locharbriggs (a) and Crossland Hill (b) control and chemically cleaned samples.

A shift in porosity distribution is clearly observed in both sandstones after chemical cleaning. Before cleaning, the Locharbriggs main porosity is distributed between 10-60 μm but this region is clearly reduced after the cleaning treatment. In addition there appears to be an enhancement of pore sizes post-cleaning in the coarser region between 200-500 μm.

Creation of new pores between 200-500 μm was also observed post-cleaning in the Crossland sandstone type, which otherwise maintain a similar pore distribution pattern.

The action of cleaning therefore creates larger pore sizes in both sandstones, however the extent to which the coarse pore distribution is increased is dependant on the sandstone type. Cleaning may also fill the finer pores sizes if suitable minerals are available for reaction, for example clays in the Locharbriggs sandstone.

5.2 Investigation of soluble salts residuals after chemical cleaning

5.2.1 Depth analysis studies

The ions selected for the chemical analysis (sodium, potassium, magnesium, sulphate, nitrate, chloride and fluoride) represent the main indicators of which type of weathering process, associated with soluble salts, has taken place.

The design of the experiment involved selection of a standard protocol described in Section 3.4. For this particular study, the average values (n=2) were taken for each of the ions at depths 0-2, 2-5, 5-10 and 10-20 mm for the Locharbriggs and 0-2, 2-5 and 5-10 mm for the Crossland Hill. The mean values and standard deviation were further used for the statistical treatment of the results (Appendix 5.2).

The percentage concentration change of the soluble ions before and after chemical cleaning was calculated at each depth (0-2, 2-5, 5-10 and 10-20 mm).

The results for Lochabriggs (Figure 5.2a) show how sodium and fluoride were introduced in the stone after chemical cleaning throughout the depth profile. Chloride and sulphate were removed but potassium increased, probably as a consequence of the weathering of feldspars and clays. Nitrate and magnesium concentrations showed no change after cleaning.

The mineralogy of Locharbriggs sandstone is characterised by the presence of clays as well as feldspars (Section 4.1). The possible effect of NaOH and HF on these aluminosilicate minerals is the dissolution of minerals with subsequent mobilisation of the cations, sodium, potassium and magnesium (Section 4.4).

Crossland Hill sandstone (Figure 5.2b) presented a similar profile for fluoride which remains at 10mm depth. However, sodium is only clearly observed at the near surface, and only a very small proportion is present after 2 mm. This cannot be explained by the different size in atomic radio (fluoride, 1.25 Å and sodium, 1.10 Å) or the concentration of these elements in the cleaning agents (fluoride, 1.0 M and sodium, 1.5 M). The low percentage change with cleaning can be explained if sodium forms a low solubility salt near-surface, for example Na_2SO_4 (solubility, 4.8 g/ml) which would then have a low tendency to migrate to-depth because of the low porosity of the Crossland sandstone instead precipitates as efflorescence on the surface. Nitrates and chlorides are removed after cleaning and sulphate is only observed at the near-surface. Potassium is probably released from feldspars and clays, especially at the near-surface which is subject to greatest attack by the cleaning agents.

In this experiment the use of different depths is a controlled factor since the depths were selected prior to the start of the measurements. The random factor introduces uncontrolled variation caused by slight differences in the drilling technique or the extraction of soluble ions into deionised water. Estimation of the variance will test whether the depth-to-depth variation is significantly greater than the variation due to the random error of measurement.

Statistical analysis of the results involved comparison of means and the method selected was the one-way ANOVA test (Section 3.7). In order to test whether the percentage change with cleaning differed significantly with depth, the dependent variables (ion concentrations) were compared for each between-subject variable (depth) (Appendix 5.4). The analysis of variance was calculated for each ion and the results for both sandstones are presented in Table 5.2. One tailed F-test is used, $F_{3,4}$= 6.59 (P=0.05, one-tail test) for Locharbriggs and $F_{2,3}$= 9.552 (P=0.05, one-tail test) for Crossland Hill. A significance test at the P=0.05 level involves a 5% risk that a null hypothesis will be rejected even though it is true. The results indicate that the percentage change on the concentration of ions extracted differs significantly at different depths for both sandstones. The differences are explained by changing the control factor depth and not by random error (i.e., the results are not an artefact of the sampling and the treatment methods).

Table 5.2 Comparison of means using one-way ANOVA test.

Ion	**Locharbriggs** $F_{3,4}$	**Crossland Hill** $F_{2,3}$
Chloride	146807	78394
Sulphate	410643	32755
Nitrate	620860	145
Fluoride	7803	3264
Sodium	9444	766382
Potassium	38303	404492
Magnesium	na	na

na = not available

The correlation coefficients for the Locharbriggs sandstone (n=8), indicated a strong correlation between fluoride with potassium (0.8865). This correlation (Table 5.3) implies a possible effect of cleaning in the dissolution of feldspars and clays.

The Crossland Hill sandstone analysis presented some high correlation coefficients as well. In this case fluoride showed a strong correlation with potassium (0.9724). Sodium and chloride are highly correlated (0.9914) while sulphate correlated negatively with sodium (-0.9915). Other results can be observed in Table 5.4. In this case, the correlations indicate the effects of chemical cleaning in the dissolution of micas and the existence of a salt load, previous to the chemical cleaning, which has not been removed by cleaning. The initial origin of these salt loadings (NaCl and Na_2SO_4) is most probably of external origin such as urban atmospheric and seawater aerosol deposition.

In general, ionic species present in the sandstone such as magnesium, potassium, sodium and calcium have different solubility product for their fluoride and fluorosilicate salts (Howe Grant, 1995). When there is only slight aluminium substitution in the clay lattice, cation concentration in solution will be small and the solubility limit of the salt is not reached. On the other hand, in the case of feldspars (albite or microcline), large amounts of sodium and potassium will go into solution and precipitate as KF (solubility, 49.6 g/100g) and NaF (solubility, 4.2 g/100g).

Table 5.3 Correlation coefficients for Locharbriggs sandstone after chemical cleaning (n = 8).

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	0.4544	-0.8496	0.0359	-0.4419	0.8565*
Fluoride	0.4544	1.0000	-0.0337	0.8865	0.5547	0.2900
Nitrate	-0.8496	-0.0337	1.0000	0.2826	0.8126*	-0.5960
Potassium	0.0359	0.8865*	0.2826	1.0000	0.7517*	-0.1841
Sodium	-0.4419	0.5547	0.8126*	0.7517	1.0000	-0.3263
Sulphate	0.8565*	0.2900	-0.5960	-0.1841	-0.3263	1.0000

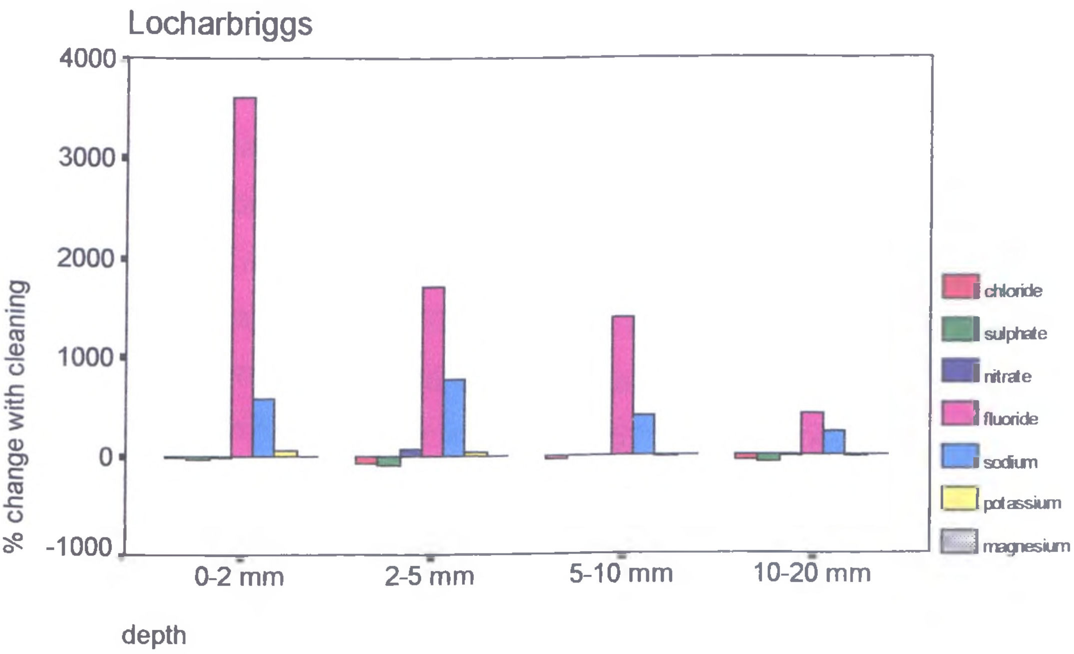
**P<0.001; *P<0.05; other values P>>0.05.

Table 5.4 Correlation coeficients for Crossland Hill sandstone after chemical cleaning (n = 8).

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	0.9072*	-0.7017	0.7849	0.9914**	-0.9660*
Fluoride	0.9072*	1.0000	-0.9333**	0.9724**	0.9545*	-0.9849**
Nitrate	-0.7017	-0.9333	1.0000	-0.9877**	-0.7885	0.8607*
Potassium	0.7849*	0.9724*	-0.9877**	1.0000	0.8592**	-0.9183**
Sodium	0.9914**	0.9545*	-0.7885	0.8592*	1.0000	-0.9915**
Sulphate	-0.9660*	-0.9849**	0.8607*	-0.9183**	-0.9915**	1.0000

**P<0.001; *P<0.05; other values P>>0.05.

(A)



(B)

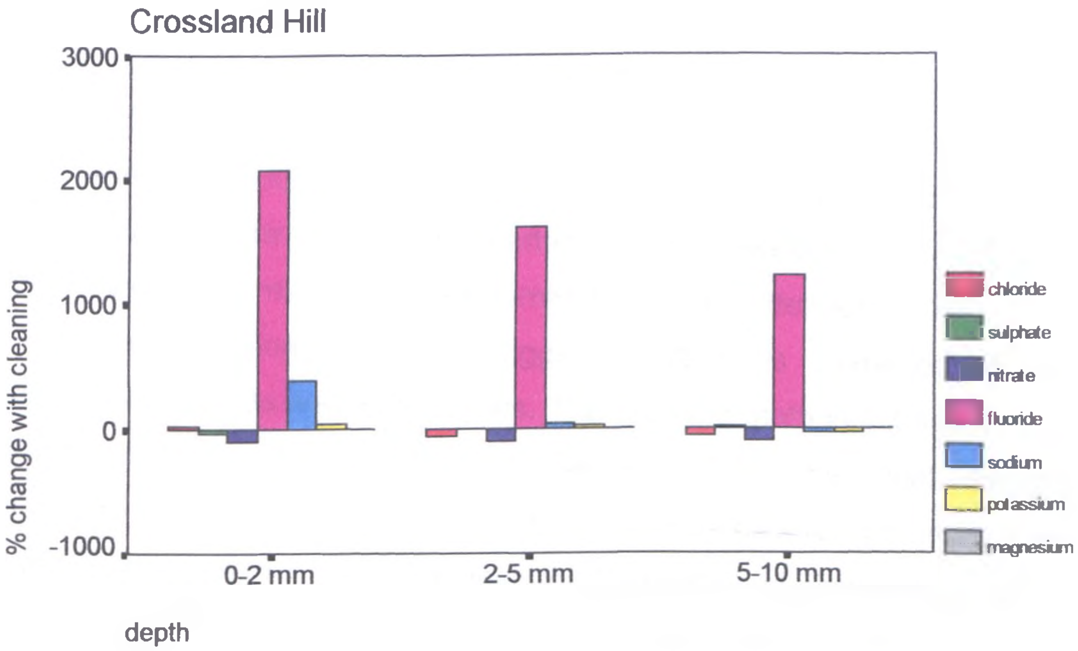


Figure 5.2a-b The percentage concentration change of the soluble ions before and after chemical cleaning was calculated at each depth (0-2, 2-5, 5-10 and 10-20 mm) for Locharbriggs (A) and (0-2, 2-5 and 5-10 mm) for Crossland Hill (B). Mean concentration before cleaning was subtracted from the mean concentration after cleaning and divided by the initial value: $(C_1 - C_0)/C_1*100$

5.2.2 Investigation of the leaching of soluble salts after chemical cleaning

The modified method was adopted from a desalination study commonly used in conservation (Section 3.4). Samples were immersed for one month in 3000 mL of deionised water in closed plastic containers, and salt removal was monitor for one month by sampling aliquots of 30 mL. Mechanical stirring was applied during all the time. One sample of each sandstone was chemically cleaned before immersion and another one was used as control. Two analysis were undertaken for each ion at times 0, 5, 15 and 30 days. The results were normalised by dividing them by a factor m/V, where m is the weight in grams of the stone sample and V the volume of immersion water in litres.

The ions selected for chemical analysis (sodium, potassium, magnesium, sulphate, nitrate, chloride and fluoride) represent the main indicators of weathering processes, associated with soluble salts. The percentage change on the concentrations of soluble ions leached before and after chemical cleaning over a period of 30 days was calculated for 0, 5, 15 and 30 days and the results are presented for both, Locharbriggs and Crossland Hill sandstones.

The results for Lochabriggs (Figure 5.3a) showed that all soluble ions analysed were more easily leached after chemical cleaning. The leaching order after 30 days was: magnesium>sodium>fluoride>chloride>potassium.

The mineralogy of Locharbriggs sandstone is characterised by the presence of clays as well as feldspars. The cleaning method left some residues behind, mainly sodium and fluoride (Section 5.2.1). The initial leaching of sandstone is related to the removal of residues from cleaning (fluoride) followed by the leaching of rock ions (magnesium). Sulphate and nitrate show decrease in post-cleaning leaching and therefore removal by cleaning action. The negative value for nitrate can be explained if the stone had a initially high concentration of nitrate residues present as soluble salts and these were partly washed off after cleaning. On the other hand sulphate did not change very much with cleaning which could mean it is present as low solubility salt such as sodium and magnesium sulphates and therefore more difficult to remove even after cleaning.

In the case of Crossland Hill sandstone (Figure 5.3b) most ions analysed were more easily leached after chemical cleaning. The leaching order after 30 days was: sodium ≈ fluoride ≈ potassium > magnesium > sulphate > nitrate. The increase in sodium can be explained as a consequence of the cleaning method which left soluble residues behind in the stone. The concentration of fluoride leached from the stone was less after cleaning than before cleaning. This could be explained considering there were little residues from cleaning compared to the Locharbriggs. The anions sulphate and nitrate are initially present in the stone as salt residues which are mobilised after chemical cleaning and leached out more readily. Also sulphate is a minor ingredient in the composition of the acid treatment applied. The negative value for chloride can be explained if the stone had a initial high concentration of chloride residues present as soluble salts and these were partly washed off after cleaning.

Crossland Hill sandstone has a significant content of feldspars and micas. If leaching increases the ionic content of sodium, potassium, fluoride and magnesium in water post-cleaning, then this can be explained by breakdown of feldspars and micas and transportation of those elements into solution. The leaching of little sulphate and nitrate compared to the other ions indicate these were removed by the cleaning action as in the Locharbriggs sandstone.

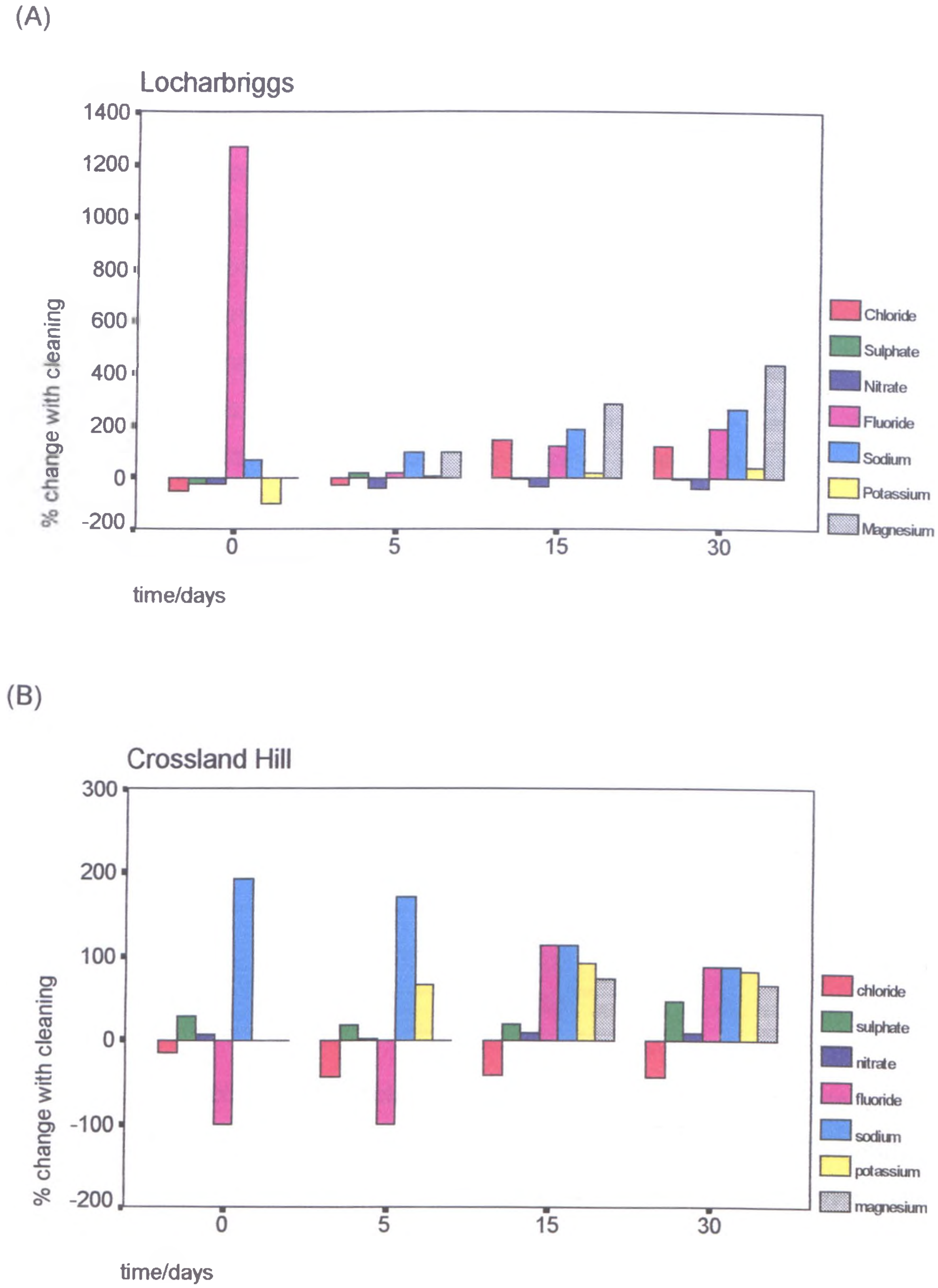


Figure 5.3a-b Mean percentage change in the leaching of soluble ions over a period of 30 days. The values were calculated as the difference between the cumulative normalised values for the cleaned and the control samples. Raw data in appendix 5.3.

Statistical analysis of the results involved comparison of means and the method selected was one-way ANOVA. In order to test whether the percentage change with cleaning differs significantly with "time", the between sample variation was compared with the within sample variation. The analysis of variance was calculated for each ion and the results for both sandstones are presented in Table 5.5. One tailed F-test is used, $F_{3,4}$= 6.59 (P=0.05, one-tail test) for Locharbriggs and $F_{3,4}$= 9.552 (P=0.05, one-tail test) for Crossland Hill. The results indicated a significant difference between the sample means for both sandstones. Therefore altering the control factor "time" lead to a significance difference between the mean values obtained and these differences are not related to random error (i.e. the results are not an artefact of the sampling and the treatment methods).

Table 5.5 Comparison of means using one-way ANOVA test.

Ion	**Locharbriggs** $F_{3,4}$	**Crossland Hill** $F_{2,3}$
Chloride	840150	4842
Sulphate	20250	1230
Nitrate	4947	939
Fluoride	1.73	101900
Sodium	3127	170
Potassium	92409	6902
Magnesium	1398224	2336

The correlation coefficients for the Locharbriggs sandstone (n=8), indicated a strong correlation between chloride with sodium (0.8866) and magnesium (0.8999). Nitrate correlated negatively with potassium (-0.9036). These correlations (Table 5.6) imply the existence of a salt load, previous to the chemical cleaning, which will be mobilised and leached out the stone. The identification of the origin of the salt species (e.g. NaCl, $MgCl_2$ or KNO_3) is difficult but the most likely source would be external (atmospheric emissions and seawater aerosols).

The Crossland Hill sandstone presented high correlation coefficients as well. In this case, fluoride showed a strong correlation with magnesium (0.9996) and sodium (-0.9374). Chloride correlated negatively with potassium (-0.9510).

Other results can be observed in Table 5.7. In this case the correlations indicate the effects of chemical cleaning in the dissolution of micas (Mg-F) and the presence of residues from cleaning (Na-F).

Table 5.6 Correlation coefficients for Locharbriggs sandstone after chemical cleaning (n = 8).

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	-0.4172	-0.3860*	0.7326	0.8866*	-0.0086
Fluoride	-0.4172	1.0000	0.7180	-0.7044*	-0.4254	-0.6204
Magnesium	0.8999*	-0.4607	-0.5511	0.8458*	0.9964**	0.0854
Nitrate	-0.3860	0.7180*	1.0000	-0.9036*	-0.4924	-0.8732
Potassium	0.7326*	-0.7044**	-0.9036*	1.0000	0.8028*	0.6022
Sodium	-0.8866*	-0.4254	-0.4924**	0.8028*	1.0000	0.0130
Sulphate	-0.0086	-0.6204	-0.8732	0.6022	0.0130	1.0000

**P<0.001; *P<0.05; other values P>>0.05.

Table 5.7 Correlation coefficients for Crossland Hill sandstone after chemical cleaning (n = 8).

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	-0.5344	0.0666	-0.9510**	0.6719	-0.0053
Fluoride	-0.5344	1.0000	0.8032*	0.7545*	-0.9374**	0.3393
Magnesium	-0.5360	0.9996**	0.8031*	0.7545*	-0.9406**	0.3491
Nitrate	0.0666	0.8032*	1.0000	0.2162	-0.6591	0.4818
Potassium	-0.9510**	0.7544*	0.2162	1.0000	-0.8101*	0.0268
Sodium	0.6719	-0.9374**	-0.6591	-0.8161**	1.0000	-0.5211
Sulphate	-0.0053	0.3393	0.4818	0.0268	-0.5211	1.0000

**P<0.001; *P<0.05; other values P>>0.05.

5.3 Investigation of colour changes after chemical cleaning

The colour analysis of the stone surfaces was done using a chroma-meter (Minolta colour meter CR-200). L (brightness) measures the lightness level on a scale of 0% (black) to 100% (white); a (green to red) and b (blue to yellow) are chromaticity co-ordinates, 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). The average values for the three components were compared before and after cleaning of the stone surfaces. The mean values and standard deviation for both sandstones, Locharbriggs and Crossland Hill, are reported in Table 5.8.

Table 5.8 The mean and standard deviation values for L (brightness), a (green to red) and b (blue to yellow) both sandstones before and after chemical cleaning.

CHANGES WITH CHEMICAL CLEANING							
Locharbriggs	L	a	b	**Crossland Hill**	L	a	b
Before cleaning	59.30±0.32	4.77±0.79	10.37±1.15	Before cleaning	64.88±0.476	0.64±0.17	11.93±1.22
After cleaning	60.78±0.29	5.15±0.88	11.35±1.05	After cleaning	66.56±0.41	0.87±0.19	12.66±1.09

The results above indicated a slight increase in the brightness (L) and green to red (a) after chemical cleaning for the two sandstones. The changes in the brightness component (L) are a consequence of the removal of the soiling on the stone surface, and are as might be expected.

The data confirm that changes in colour do occur on cleaning and the variation is dependant on the sandstone type. This has implications for the aesthetic quality of cleaned sandstone blocks but it is not a useful guide to relative decay rates.

5.4 Scanning Electron Microscopy

This technique enabled small-scale examination of the surface of the stone across areas of few microns (Section 3.4). Small samples of control and chemically cleaned sandstones were coated with a thin layer of Au/Pd prior to examination. The samples were firstly treated with NaOH and HF independently to see the effects of these two agents separately on the minerals and compared with a control treated with deionised water. The samples were then chemically cleaned (Section 3.3) and compared with a control treated with deionised water only.

The Locharbriggs control sample clearly showed the clay coating on the quartz surface (Plate 5.1a). When this sample is treated with NaOH, it resulted in the deposition of Na-containing salts on the surface of quartzs and micas (Plate 5.1b). These deposits gave a concave morphology. Application of HF did not result in the attack of quartzs or feldspars and even clays (smectite) remained in some areas of the stone (Plate 5.1c). Analysis of chemical elements by energy dispersive system (EDX analysis) indicated the presence of Si, Al, K, Na and Fe on the selected mineral (Appendix 5.5).

When the Locharbriggs samples were examined post-cleaning (NaOH followed by HF), it was observed a partial removal of the soiling layer and the presence of smectite clay still covering the surface of the quartz grains (Plate 5.1d-e).

The Crossland Hill control sample presented some soiling on the surface and intergranulary clays were observed (Plate 5.2a). After treatment with NaOH, deposits of the same morphology as in the Locharbriggs sandstone were observed on the surface of the quartz grains (Plate 5.2b). Application of HF resulted in removal of some surface debris and revealed the presence of an iron oxide mineral (e.g. goethite) which may be a weathering product already present pre-cleaning (Plate 5.2c). The analysis of these crystals by EDX only showed peaks due to Si, Al, and Fe (Appendix 5.5).

The Crossland Hill samples appeared heavily soiled before cleaning (Plate 5.2d). Application of the cleaning treatment (NaOH followed by HF) revealed cleaned mineral grains (Plate 5.2e-f) of quartz and mica. No signs of etching or salt deposits were observed.

Plate 5.1a-c SEM photomicrograph of the Locharbriggs sandstone: (A) before cleaning; (B) after NaOH treatment and (C) after HF treatment.

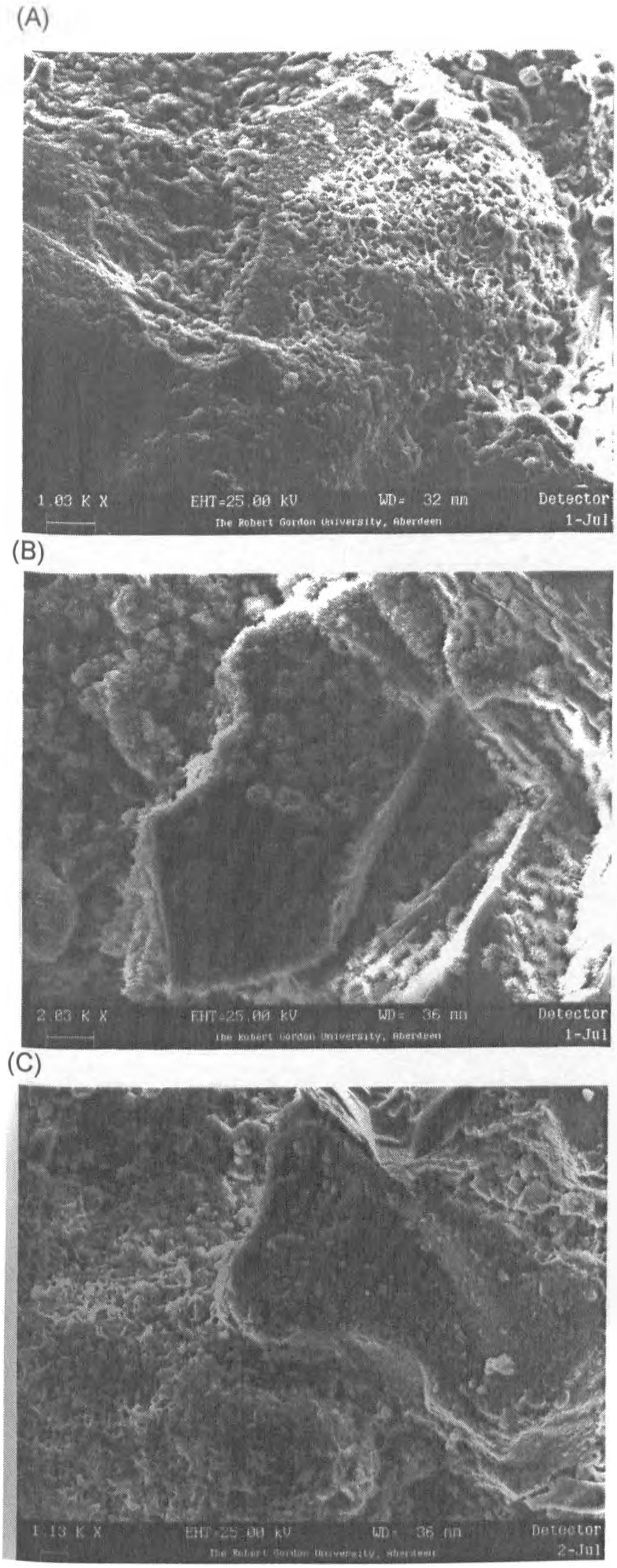


Plate 5.1d SEM photomicrograph of the Locharbriggs sandstone showing remains of smectite clay on the surface of quartz grains after chemical cleaning.

(D)

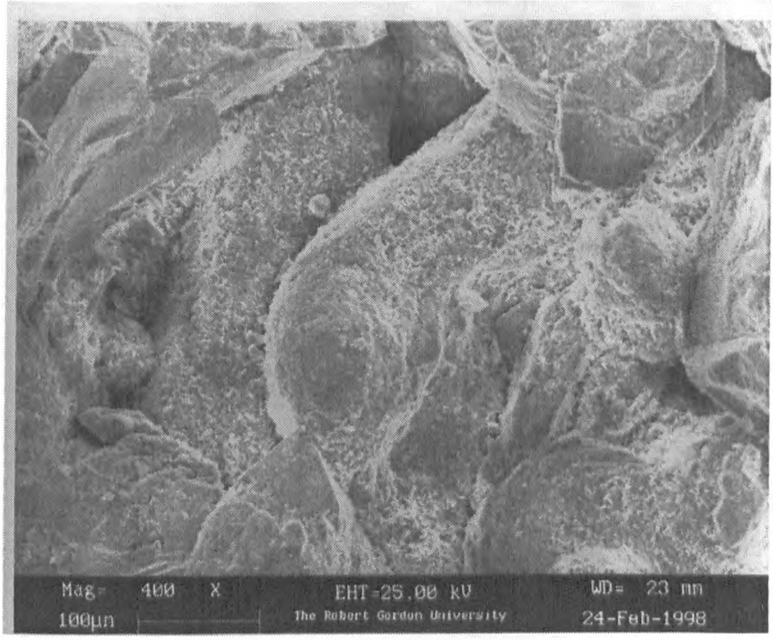


Plate 5.1e SEM photomicrograph of the Locharbriggs sandstone showing crystalline deposits in the pore network after chemical cleaning.

(E)

Plate 5.2a-c SEM photomicrograph of the Crossland Hill sandstone: (A) before cleaning; (B) after NaOH teatment and (C) after HF treatment.

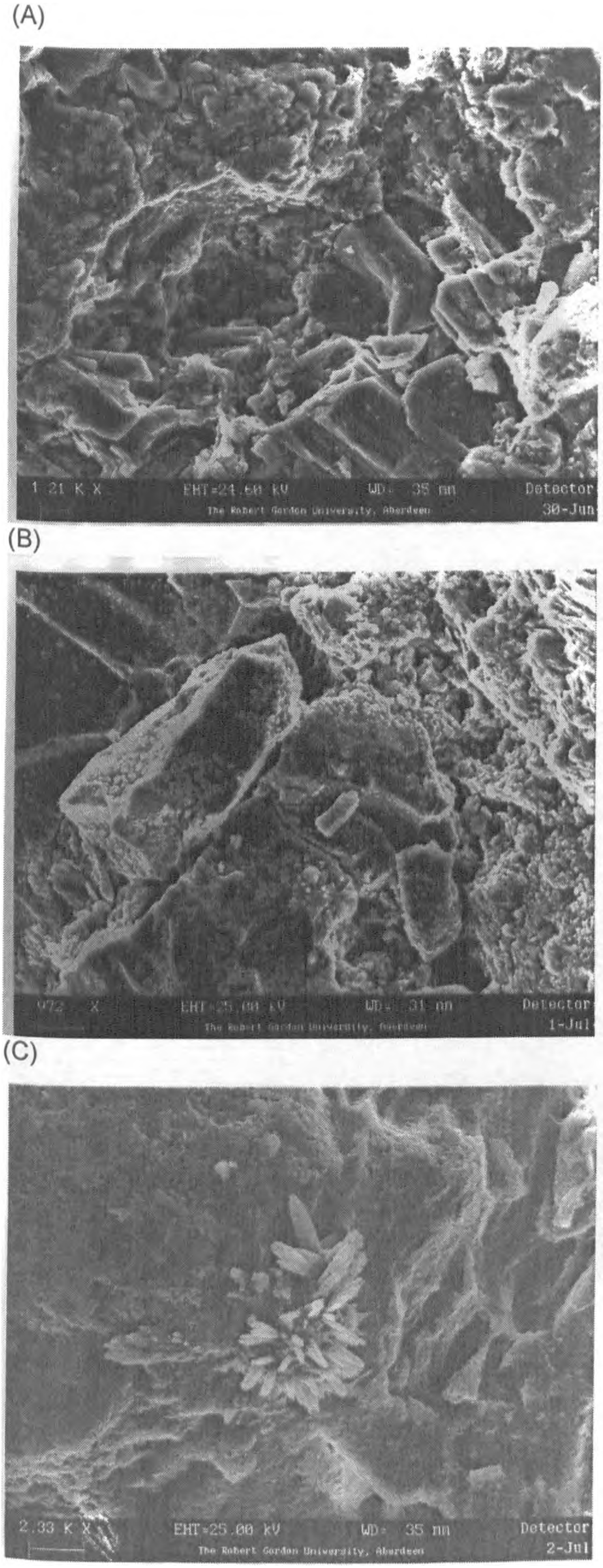
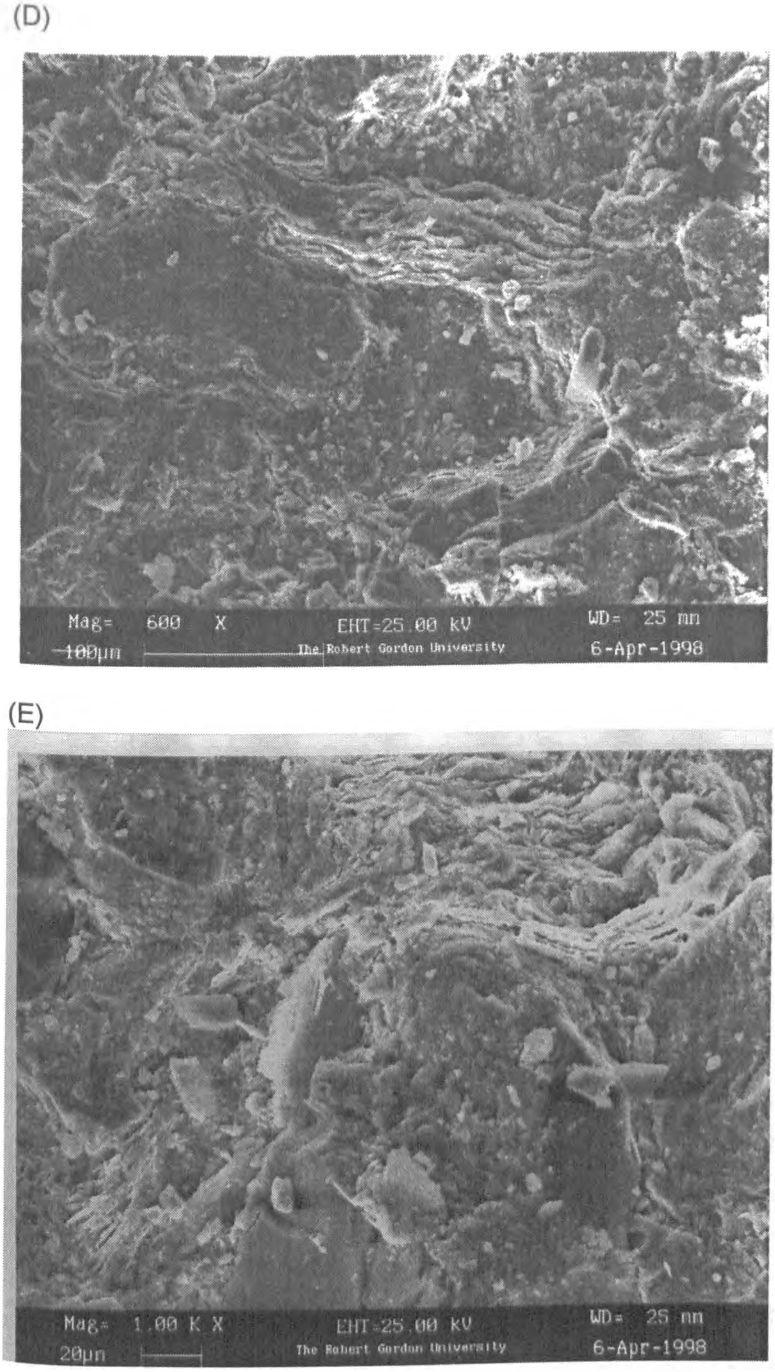


Plate 5.2d-e SEM photomicrograph of the Crossland Hill sandstone after chemical cleaning showing mineral grains of quartz and mica.



5.5 Conclusions

Chemical cleaning had an effect in the porosity distribution of the two sandstones. The changes produced after cleaning sandstone with an acid-based system were reported previously in other studies but in all cases the opening of pores and therefore the increase in porosity was the general observation. The results presented here showed that overall porosity and porosity distribution will change in accordance to the type of minerals involved and the reactions between these minerals and the chemicals applied. The reaction between an acid such as HF, and a clay, such as kaolinite will very readily produce silica and aluminium cations. These reaction products could deposit as insoluble aluminium and silicon forms and probably block the pore space of the Locharbriggs sandstone. The same cleaning process on the Crossland Hill lead to an opening of the pore system and therefore removal of soiling.

Both sandstones increased their porosity between 200-500 μm and the smaller pores sizes remained either unchanged (Crossland Hill) or decreased (Locharbriggs). This means that deposition of residues from cleaning filled in the smaller pores first and potential damage to the stone due to crystallisation of these secondary salts will occur at this level.

The cleaning method left soluble residues behind, mainly sodium and fluoride. Although these levels tend to decrease with depth, there were still present at depths of 20 mm (Figure 5.2a-b). Cleaning also had an effect on the release of ions such as potassium which can only have their origin in the mineral components.

In both sandstones, fluoride and sodium were easily leached after acid-based cleaning, especially from Locharbriggs at time 0 days. The nitrate and sulphate concentrations in the leaching waters did not vary significantly with the cleaning process in neither of the sandstones. In the Locharbriggs stone (Figure 5.3a) chloride increased with time after cleaning. In the Crossland stone (Figure 5.3b) chloride decreased after cleaning. On the other hand, magnesium and potassium concentrations in water increased for both sandstones. Also from day 15 to 30, the systems seemed to reach an equilibrium in the leaching trends.

From the leaching/depth profile results presented above it can be concluded that initially both sandstones present considerable amounts of soluble ions/cleaning residues. These may include low solubility stable salts such as sulphates of sodium and magnesium, anhydrous stable salts such as potassium and sodium chlorides and different hydrous salts such as sodium and magnesium sulphates. Chemical displacement reactions are likely to occur within the stone and hydration of salts will occur depending on the water content in the stone. Additionally, the source of the cations can be related to the mineral oxides contained within the stone samples. These cations could be leached out of the stone matrix by exchange mechanisms which can occur when cations become displaced from their binding sites within the matrix by other cations or by dissolution from the minerals

The fact that the percentage changes of soluble ions leached can only be attributed to the cleaning method itself indicate that weathering processes might be accelerated after such cleaning method.

Statistical analysis indicated that the percentage change with cleaning on the concentration of ions extracted differs significantly at different depths and times for both sandstones.

6 SALT WEATHERING STUDIES ON CHEMICAL CLEANED SANDSTONES

Sample cores of sandstone (40 mm height by 20 mm diameter) were partially immersed in salt solutions of 0.1M NaCl and 0.1 M Na_2SO_4 for four months. This method described by Sperling and Cooke (1985) allows capillary rise, concentration by evaporation and crystallisation of the salt in a narrow zone of the sample. It also simulates the situation in which lower walls of buildings are affected by capillary rise and therefore exposed to salt weathering.

The experiments were carried out at room temperature and each core was immersed in an independent closed plastic container and in all cases, the immersion in salt solutions was at a constant depth of 1 mm. This situation intended to simulate a single damage process due solely to crystallisation pressure.

6.1 Investigation of the interaction of salts and porosity distribution

The changes in porosity and pore size distribution were evaluated by means of mercury porosimetry.

When Locharbriggs samples were exposed to the action of salt solutions the overall porosity increased, compared to the water control, with Na_2SO_4 the salt having the greatest effect, followed by NaCl and seawater. For the Crossland Hill sandstone, the percentage change in overall porosity ranged from 0.5-1.0% and decreased in all cases (Table 6.1).

Table 6.1 Porosities of sandstones after immersion in salt solution for 4 months and percentage change when compared to the initial porosity prior immersion. Raw data in Appendix 6.1.

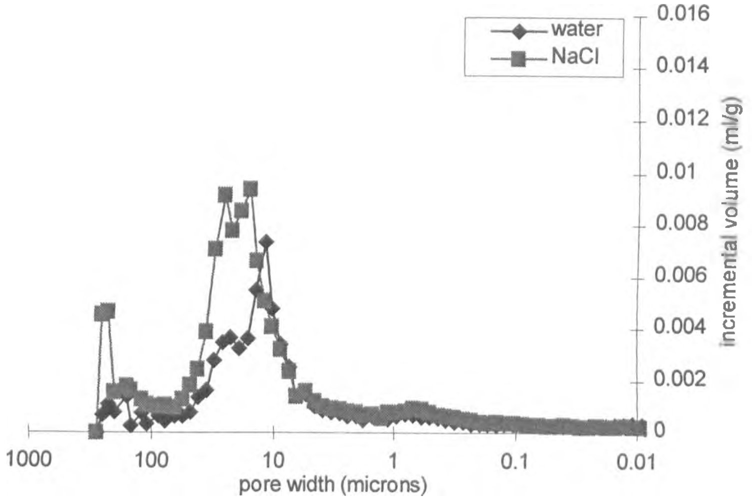
Sandstone	Treatment	Mean porosity, %	sd	Δporosity, %
Locharbriggs	Water	20.57	0.25	2.34
	NaCl	23.44	0.31	5.21
	Na_2SO_4	25	0.29	6.77
	Seawater	22.19	0.51	3.96
Crossland	Water	10.62	0.47	-1.91
	NaCl	9.90	0.67	-2.63
	Na_2SO_4	8.84	0.38	-3.69
	Seawater	9.37	0.46	-3.16

For the Locharbriggs sandstone, the differences in porosity distribution occurred at 10-80 μm and in the coarser region between 100-500 μm (Figure 6.1a-c). The total volume of these pore sizes was higher for core samples immersed in Na_2SO_4 and NaCl, consistent with the creation of new porosity. Seawater (0.3M NaCl and 0.03M Na_2SO_4) did not affect the porosity in this region (100-500 μm) but it was more aggressive than 0.1M NaCl between 10-80 μm. This region was especially affected by the three systems when compared to the control sample in deionised water.

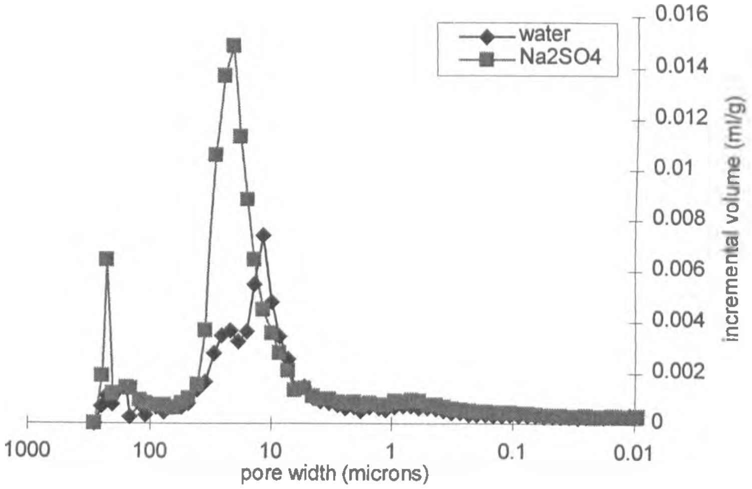
To explain these results, it can be considered that the 0.1M solutions contributed little towards crystallisation processes within the stone pore system, instead the salts simply deposited on the surface of the samples as efflorescences. Similar observations were described by Lewin (1982) in laboratory test using stone prisms to simulate rinsing damp. Furthermore, it can be suggested that the ionic diffusion from the stone is of the same order or larger than the capillary transport of ions into the stone. In the first case, there is the same salt concentration/gradient and salts cannot dilute so they effloresce on the surface. In the second case, the movement of soluble ions into solutions would open new porosity. Calculations by Snethlage and Wendler (1997) using the Fick's first law did in fact show that the transport of ions to the surface through capillary water flow and the migration back into the interior of the stone into the diluted solution can reach the same order of magnitude for a range of concentrations.

A second mechanism to explain the increase in porosity between 10-80 μm can be related to the changes in the distance from grain to grain. Experimental studies on hydric dilatation of sandstone partially immersed in a solution of saturated gypsum (Snethlage and Wendler, 1997) indicated that the hydric dilatation in the presence of salts is always larger than in water. This was explained considering gypsum deposited between the grains in the stone blocking the pore system and preventing the free displacement of grains, which eventually takes place with the consequent irreversible dilatation. This effect would translate in a opening of porosity.

(A)


water
NaCl
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
incremental volume (ml/g)
1000
100
10
1
0.1
0.01
pore width (microns)

(B)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Na2SO4
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0.014
0.012
0.01
0.008
0.006
0.004
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incremental volume (ml/g)
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pore width (microns)

(C)

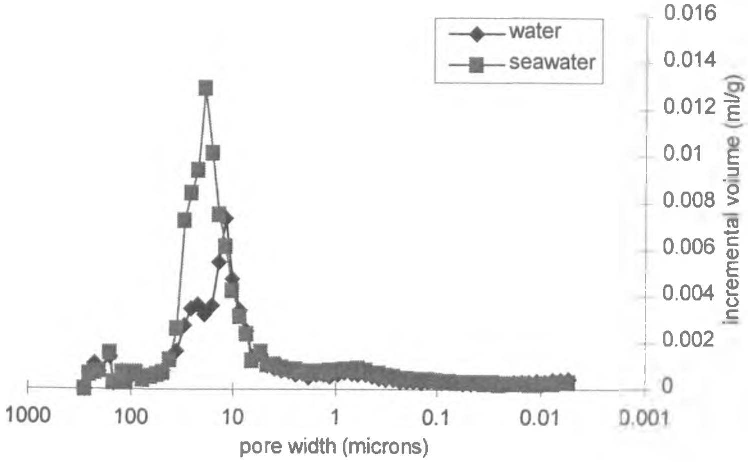
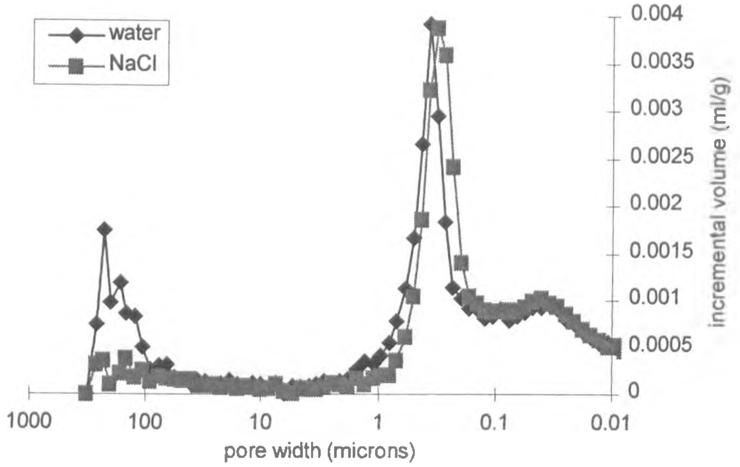


Figure 6.1a-c Pore size distribution for Locharbriggs core samples after partial immersion in 0.1M NaCl (a), Na_2SO_4 0.1M (b) and artificial seawater (c) solutions for 4 months. All graphs compared to the porosity distribution of the control sample immersed in deionised water.

For the Crossland Hill samples, the overall porosity decreased when compared to the control in deionised water although these changes were small (0.5-1%) and they concentrated on the coarser region between 100-500 μm (Figure 6.2a-c).

These results are in agreement with previous work by Theoulakis and Moroupolou (1997) who showed how NaCl fills the coarse pores (> 10 μm) first and then it creates a pressure which can lead either to the continuation of the crystallisation by filling the smaller pores or to the disruption of the pore walls. These results also agree with the thermodynamic model proposed by Wellman and Wilson (1965) who concluded that salt crystallisation takes place initially in the larger pores from solution being supplied from the smaller capillaries.

(A)



water
NaCl
0.004
0.0035
0.003
0.0025
0.002
0.0015
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incremental volume (ml/g)
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0.1
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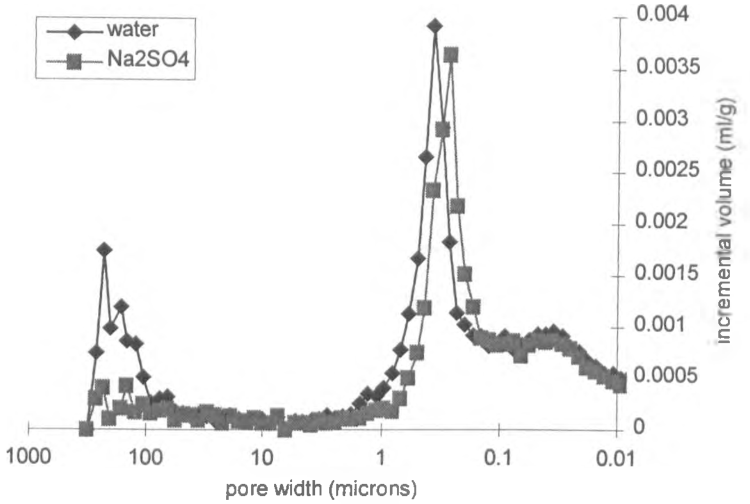
pore width (microns)

(B)



water
Na2SO4
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0.003
0.0025
0.002
0.0015
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incremental volume (ml/g)
1000
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10
1
0.1
0.01
pore width (microns)

(C)

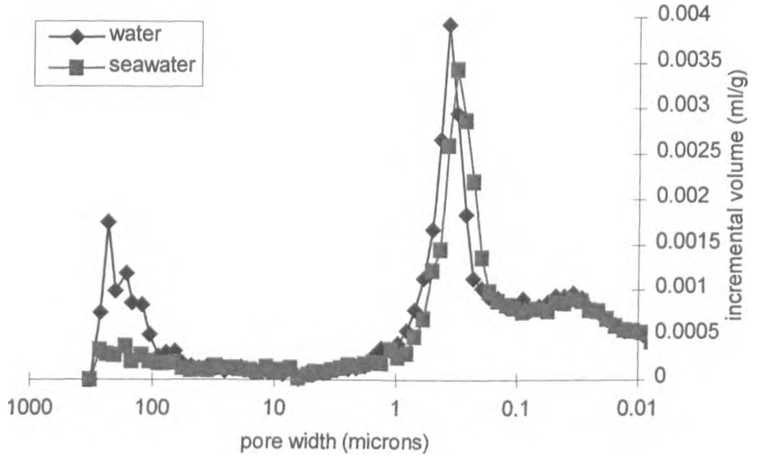


Figure 6.2a-c Pore size distribution for Crossland Hill core samples after partial immersion in 0.1M, NaCl (a); 0.1M, Na_2SO_4 (b) and artificial seawater (c) solutions for 4 months. All graphs compared to the porosity distribution of the control sample immersed in deionised water.

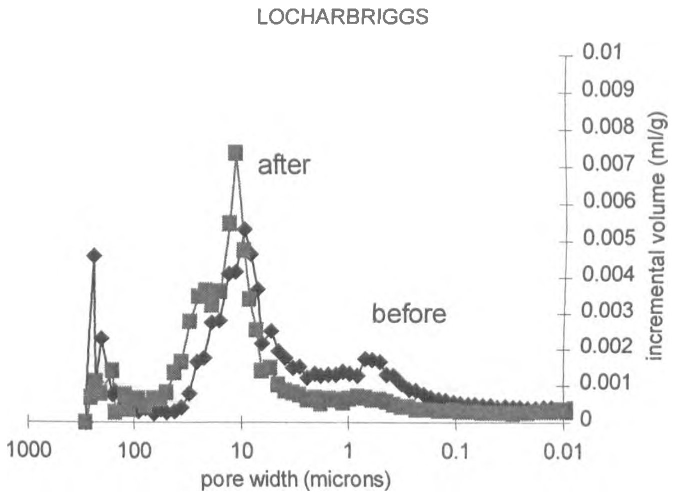
6.1.1 Summary

Chemically cleaned sandstones partially immersed in salt solutions (NaCl, Na_2SO_4 and seawater) for four months experienced a change in the porosity distribution when compared to the control samples immersed in deionised water.

In the Locharbriggs sandstone, the initial porosity (18.23%) increased after partial immersion in both the free and the salt-contaminated systems (Figure 6.3 a-b). The ionic transfer of soluble salts into the solution together with a dilatation and further irreversible expansion of the stone could explain the increase in porosity of the Locharbriggs sandstone. The presence of soluble residues prior to the partial immersion in solution was investigated in Chapter 5. For Locharbriggs, sodium and fluoride were introduced up to depths of 20 mm after chemical cleaning. If their concentrations within the stone pore system were higher than the solution then the ionic diffusion would take place over the transport of solution to the stone. Appendix 5.1 shows the results for the depth profiling after chemical cleaning. The concentrations for sodium and fluoride are 0.08M and 0.13M respectively. Therefore, the opening of porosity can be explained by dissolution reactions which result in the movement of ions from the sandstone back into solution. Additionally, hydric dilatation would contribute to this opening and it would also explain the differences between immersion in control water and the salt-contaminated solutions.

In the Crossland Hill sandstone, the initial porosity (12.5%) decreased after partial immersion in both free and salt-contaminated systems (Figure 6.4a-b) therefore precipitation reactions took place within the pore system. Preferential crystallisation was located at the larger pores (100-500 μm). These results agree with the thermodynamic model proposed by Wellman and Wilson (1965) who concluded that salt crystallisation takes place initially in the larger pores from solution being supplied from the smaller capillaries.

(A)



(B)

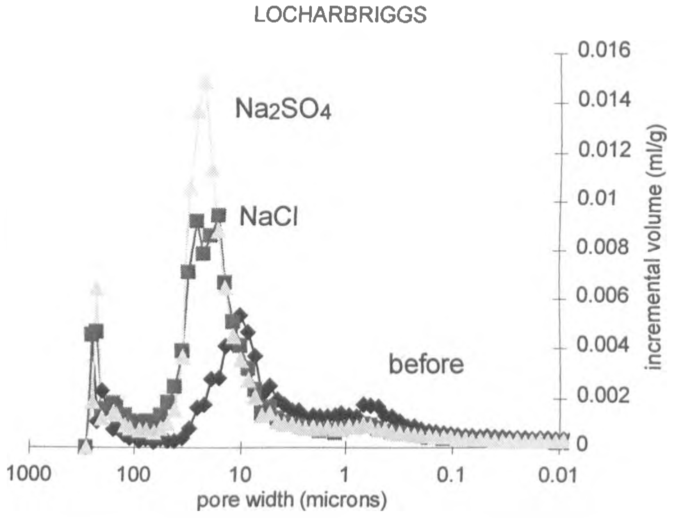


Figure 6.3a-b Porosity distribution of Locharbriggs before and after partial immersion in deionised water (a) and salt-contaminated solutions (0.1M NaCl and 0.1M Na_2SO_4) (b).

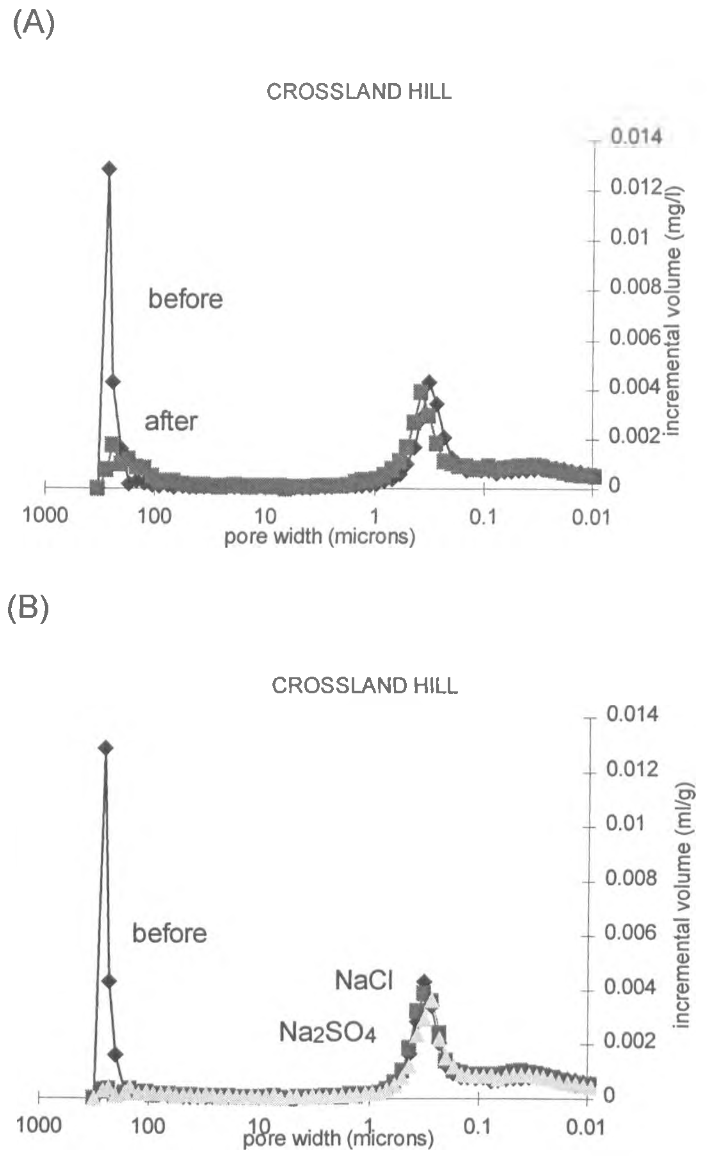


Figure 6.4a-b Porosity distribution of Crossland Hill before and after partial immersion in deionised water (a) and salt-contaminated solutions (0.1M NaCl and 0.1M Na_2SO_4) (b).

6.2 Investigation of the tensile strength

The hypothesis of crystallisation pressure as the damaging factor of salt decay was considered here to explain the mechanisms by which salts can induce damage in chemically cleaned sandstone. The Fitzner and Snethlage model (1982) was used to calculate crystallisation pressures. According to these authors, salts crystals grow preferentially in the largest pores and the salt solution is withdrawn from the smaller pores. When a coarse pore is filled with crystals, crystallisation continues in the smaller pores connected to it and a crystallisation pressure is then developed.

The tensile strength of the samples was determined experimentally by the classical uni-axial compression method (ASTM). Data were collected from three specimens of each sample and tensile strength, σt, was calculated using the equation: $\sigma t = 2F/ \pi Dt$ (La Iglesia, 1997), where F is the load at failure and D and t are the diameter and the thickness of the test specimen, respectively (Table 6.2).

Table 6.2 Calculated tensile strength by compression for the two sandstone types. Raw data in Appendix 6.2.

SALT SYSTEM (mol/L)	LOCHARBRIGGS (MPa)	CROSSLAND HILL (MPa)
NaCl, 0.1M	1.62	2.42
Na_2SO_4, 0.1M	1.57	2.41
Seawater*	1.57	2.41
Deionised water	1.14	2.38

**Artificial seawater was prepared in the lab (NaCl, 0.36M; Na_2SO_4 0.029M).*

The next step involved calculation of the theoretical and effective pressure for the two cleaned sandstones after immersion in NaCl and Na_2SO_4 solutions.

The method employed here to estimate the crystallisation pressures developed in the two sandstones under study has already been used by other researches (Gauri *et al.*, 1986; Rossi-Manaresi and Tucci, 1989). The pores are classified as a function of their radius (expressed in μm): class I, $r < 0.1$; class II, $0.1 < r < 1$; class III, $1 < r < 10$; class IV, $10 < r < 100$; class V, $r > 100$. The average radii for each class was calculated: 0.045, 0.45, 4.5 and 45 μm respectively. Using the data of the pore volume distribution versus pore diameter (Figure 6.5), an estimate of the percentage pore volume of each pore class was made (Table 6.3).

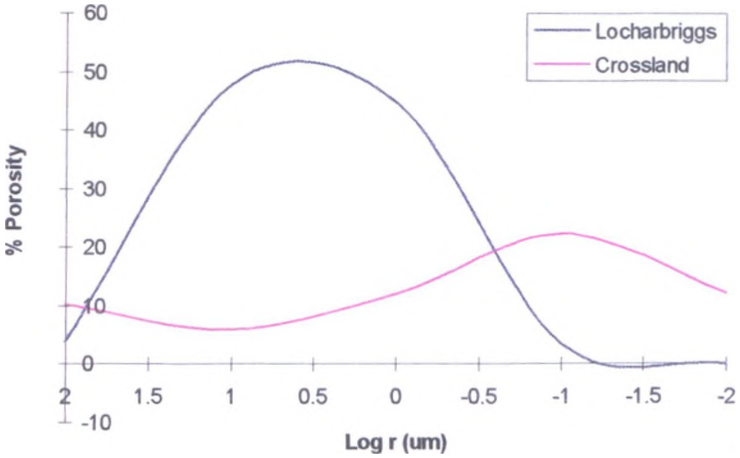


Figure 6.5 Pore-volume distribution versus pore diameter of the two sandstones.

Table 6.3 Theoretical pore volume % for the two sandstones used in the study. Calculations in Appendix 6.2.

Sample	**Porosity %**	**Class pore size**				
		I r < 0.1	II 0.1 < r < 1	III 1 < r < 10	IV 10< r <100	V r >100
Locharbriggs	18.23	1	7	27	36	29
Crossland	12.5	14	52	12	7	15

To calculate the crystallisation pressures in different pore classes, R = 45 μm was taken as a constant value to use in the following expression (Fitzner and Snethlage, 1982):

$$P = 2\sigma(1/r - 1/R) \qquad (6.2)$$

The values of the salt-solution interfacial tension, σ, for the two salt systems used in the study, NaCl (0.0727 N/m) and Na_2SO_4 (0.0728 N/m) were taken from the literature (La Iglesia, 1997). The values of the effective pressure calculated for the crystallisation of NaCl and Na_2SO_4 in the two sandstones are presented in Table 6.4.

Table 6.4 Calculated pressures (MPa) of NaCl and Na_2SO_4. Calculations in Appendix 6.3.

LOCHARBRIGGS			CROSSLAND HILL		
Pore radio	NaCl	Na_2SO_4	Pore radio	NaCl	Na_2SO_4
0.045	0.4563	0.5324	0.045	4.5942	5.3245
0.45	0.1135	0.1854	0.45	0.8347	0.8458
4.5	0.0904	0.1004	4.5	0.0135	0.0185
45	0.0065	0.0079	45	0.0018	0.0017
P total (MPa)	**0.6667**	**0.8265**	P total (MPa)	**5.4442**	**6.1905**

The sum of the effective pressure of each class represents the total pressure (tension) that the sandstones will support when the salts crystallise. These values were compared to the experimental values (Table 6.2).

The variation of pressure versus the percentage of pore filled for the two sandstones after immersion in NaCl and Na_2SO_4 is represented in Figures 6.6a-b.

The sum of the effective pressure of each class represents the total pressure (tension) that the sandstones will support when the salts crystallise. These values were compared to the experimental values (Table 6.2).

The variation of pressure versus the percentage of pore filled for the two sandstones after immersion in NaCl and Na_2SO_4 is represented in Figure 6.6a-b.

The results show that crystallisation pressure is associated with pore size distribution and in particular with the percentage of small pores (classes I to III). For example, the calculated pressures from Table 6.4 indicate that Crossland Hill is the stone most likely to undergo salt decay and it is also the one with a subtantial percentage of small pores as well as pores of larger size.

In both sandstones, 90% of the total effective pressure is developed at the microporosity level ($r < 1$ μm) and even then the values are well under the experimentally calculated tensile strength (Figure 6.6a-b).

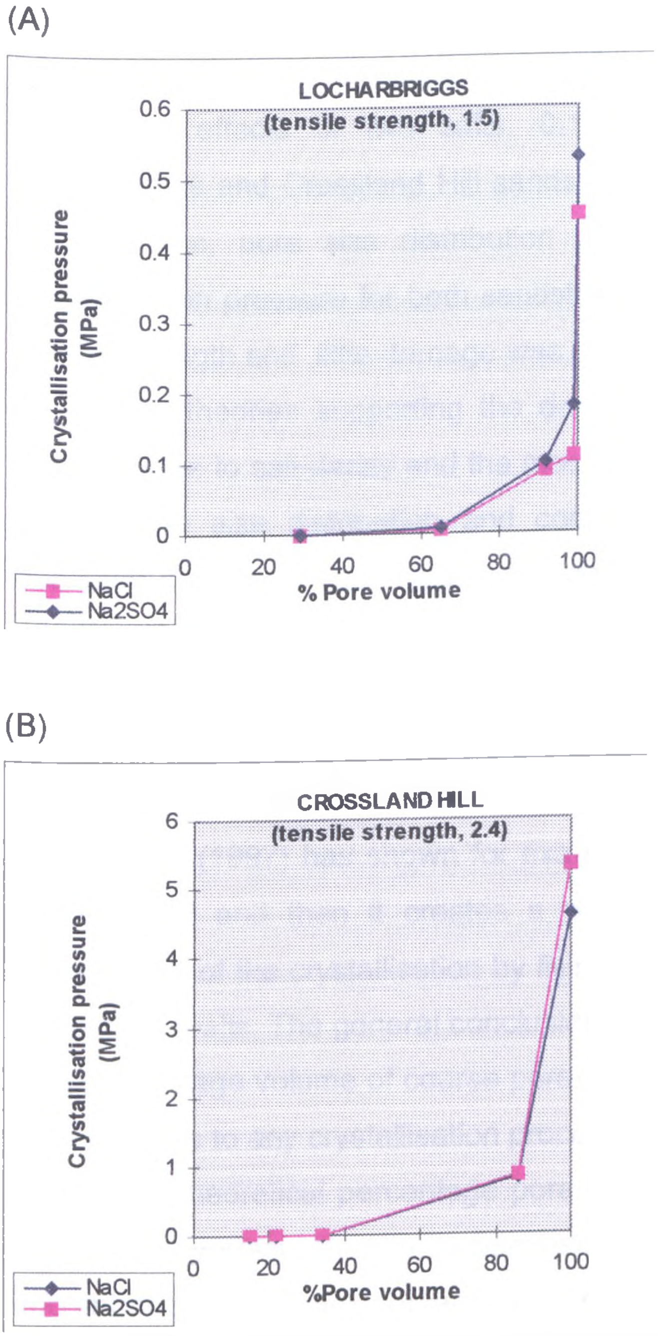


Figure 6.6a-b Estimation of crystallisation pressures for the two sandstones, Locharbriggs (a) and Crossland Hill (b), in NaCl and Na_2SO_4.

6.2.1 Summary

The effects of two salts, 0.1M NaCl and 0.1M Na_2SO_4, on the Locharbriggs and Crossland Hill sandstones, were studied as a function of the pore volume, pore size distribution and tensile strength. The calculated crystallisation pressure for both sandstones was smaller than the experimental tensile strength and little damage was caused by the two salt solutions.

The theories supporting the dependence between susceptibility of the porous stone to salt decay and the mechanical and structural parameters of the stone (pore size distribution and compressive strength) have been widely accepted (Correns, 1949; Fitzner and Snethlage, 1982; Lewin, 1982; Camuffo, 1995) and they conclude that salt decay occurs only when optimum porosity characteristic are obtained (Gauri *et al.,* 1992; Rossi-Manaresi and Tucci, 1991) and the pressure exerted by a growing crystal in a pore is a function of the supersaturation ratio (Correns, 1949). Previous work by Theoulakis and Moroupolou (1997) has shown for example that NaCl fills the coarse pores (> 10 μm) first and then it creates a pressure which can lead either to the continuation of the crystallisation by filling the smaller pores or to the disruption of the pore walls. The general conclusion from these works is that stones with a high percentage volume of coarse pores and low percentage of small pores are more durable to any crystallisation process.

The theoretical percentage pore volume of each pore class (Table 6.3) indicated important differences between Locharbriggs and Crossland Hill. For Locharbriggs, the larger percentage pore volume was distributed between 10-100 μm (36%) and for Crossland Hill this was located between 0.1-1 μm (52%).

Considering the theory (Rossi-Manaresi, 1991) that during initial crystallisation salt crystals grow selectively in pores larger than 10 μm then immersion in NaCl and Na_2SO_4 solutions should result in different effect on the Locharbriggs and Crossland Hill with a 66% and 22% volume of pores larger than 10 μm respectively. Salts would start filling in the coarse porosity of both sandstones followed by the smaller pores until the effective crystal pressure exceed the tensile strength of the stone. This process would be completed sooner in the Crossland Hill sandstone as the percentage volume is smaller.

It is observed from equation 6.2 that the pressure generated during crystallisation depends on the pore size and the salt-solution interfacial tension. This latter value was the same for the two salt systems selected and therefore differences between the two sandstones are based only in the porosity. The pressure developed for each pore class (Table 6.4) and the variation of pressure against the percentage of pores filled (Figure 6.6) indicated that the behaviour of each sandstone was different. For the Locharbriggs, samples did not develop great pressures before 60% of the pore volume was filled and even at 100%, the pressures developed were well bellow the experimental tensile compression test (1.5 MPa).

For the Crossland Hill, only considerable crystallisation pressure was reached when 90% of the pores were filled. The experimental tensile compression (2.4 MPa) was then overpassed and damage expected.

In both cases, 90% of the total effective pressure was developed at the microporosity level ($r < 1$ μm) and as expected, the value for the Crossland Hill sandstone was larger cause the percentage volume porosity at this level was also larger. These results indicate that crystallisation pressure on the chemically cleaned sandstones was only important at microporosity level and even then the values were well under the experimentally calculated tensile strength.

6.3 Conclusions

Chemically cleaned sandstones partially immersed in salt solutions (NaCl, Na_2SO_4 and seawater) for four months experienced a change in the porosity distribution when compared to the control samples immersed in deionised water and also when compared to the initial porosity prior to the immersion experiment.

When comparing results, Locharbriggs porosity increased between 20-50 μm and 100-500 μm and Crossland Hill decreased at the larger pores between 100-500 μm (Figure 6.3a-b). These changes imply a remobilization of solutes within the stone. The higher content of soluble residues after cleaning in Locharbriggs compared to Crossland Hill together with an original higher porosity could explain the tendency for the first to undergo dissolution reactions unlike the Crossland type which is well cemented by quartz overgrowths and consequently more difficult to attack. The type of reaction expected in this later case will be precipitation.

The cleaning process left soluble residues within the stone, especially sodium and fluoride, as shown by the analysis of soluble ions in Chapter 5. These were found at depths of up to 20 mm for Locharbriggs compared to only 5 mm for Crossland Hill. Partial immersion in water might have either helped remove some of these post-cleaning residues (increasing porosity) or promoting the precipitation of aluminosilicates previously dissolved (decreasing porosity). Unfortunately, no depth profile analysis of the core samples was undertaken after partial immersion and therefore it is not possible to confirm this hypothesis.

Theoretical salt damage was studied as a function of the pore volume, pore size distribution and tensile strength using Fitzner and Snethlage model (Fitzner and Snethlage, 1982). The calculated crystallisation pressure for both sandstones was smaller than the experimental tensile strength and little damage was caused by the two salt solutions. These results confirm the observations in Section 6.1, for the Locharbriggs sandstone, where it was considered that the 0.1M solutions contributed little towards crystallisation processes within the stone pore system, instead the salts simply deposited on the surface of the samples as efflorescences.

In the case of Crossland Hill, precipitation reactions within the pore system would explain the reduction in porosity and only considerable crystallisation pressure was reached when 80% of the pores were filled. The experimental tensile compression (2.4 MPa) was then overpassed and damage expected.

In this particular study, no evidences of cracking were found and although there were little evidences of salt damage for either of the two stones, the visual inspection of the samples after drying in the oven at 110°C for 24 hours allowed the examination of efflorescence patterns.

For the Locharbriggs samples, NaCl was mainly effloresced at and above the solution contact surface. Na_2SO_4 was effloresced on the top surface from which the solution evaporated. Partial immersion in seawater resulted in development of efflorescences at the surface contacting the solution. The control sample in deionised water presented a clean surface.

For the Crossland Hill samples, NaCl was evenly effloresced across the surface. Na_2SO_4 was preferentially effloresced on the top surface and seawater effloresced randomly across the surface although with more intensity at the centre of the core sample. Control sample in deionised water presented some efflorescence on the top surface.

These observations are in agreement with those reported by others authors (Lewin, 1982; Doehne, 1994) after studying the effects of crystallisation of NaCl and Na_2SO_4 on the weathering of sandstones.

7 CYCLICAL WEATHERING STUDIES

In the previous chapter, salt damage was studied after partial immersion of Locharbriggs and Crossland Hill sandstones in three salt-contaminated solutions. No RH cycling or temperature variation was promoted during the experiment and the effects of salt weathering were monitored by looking at the porosity distribution changes.

In this chapter, an experiment was set up to evaluate the effects of cyclical weathering on Locharbriggs and Crossland Hill sandstone types after single immersion in saline solutions. The purpose of the experimental work was to simulate daily wet/dry cycles based on field data from a representative Scottish environment (Metereological Office). The effects of cyclical weathering were monitored by looking at the weight and porosity distribution changes and the distribution pattern of soluble ions in depth. The porosity results were further compared to the ones in Chapter 6.

7.1 Cycling weathering after immersion in NaCl and Na_2SO_4 salts

The single-immersion technique as proposed by Goudie (1995), provided the laboratory simulation model. Three samples of each sandstone were immersed for 24 hours in 0.6 M NaCl (non-hydratable salt) and 0.4 M Na_2SO_4 (hydratable salt) and compared to a control immersed in deionised water. All the samples were exposed as prisms of certain dimensions (80 x 80 x 40 mm).

The cycle used in the BR590H cabinet (Section 3.4) represented a typical humid summer conditions, characterised by a daily variation of temperature at the stone surface and high but variable relative humidity. The daily temperature range was between 5°C and 35°C and the humidity range between 70 and 90 per cent. Samples were exposed to 24 hour cycles (12 hour of 5°C and 90 per cent humidity and 12 hour of 35°C and 70 % per cent humidity) between 7-12 weeks.

7.1.1 Weight changes

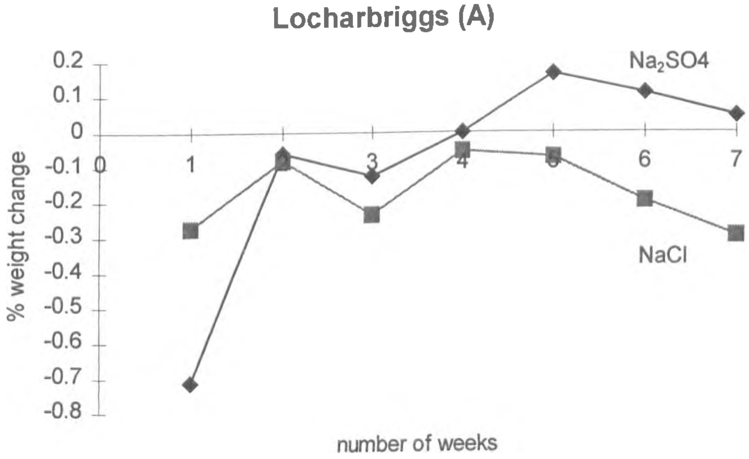
The average salt up-take after 24 hour immersion in 0.6 M NaCl and 0.4 M Na_2SO_4 was determined gravimetrically. The most effective salt was Na_2SO_4 in agreement with Goudie's work (Goudie, 1995) and it was also the most taken up into samples (Table 7.1). NaCl had little effect.

The weight changes during cyclical weathering of the salt-contaminated stones indicated a very small variation with time (Figure 7.1a-b).

This could be explained by the continuous precipitation and dissolution of the salts or by mechanical lost. These mechanisms, chemical and physical, have different effects depending on the sandstone type. The weight change data are shown as percentage weight change relative to the relevant control sample. Using relative weight change removes from the result any weight change which is not due to the RH/T cycles. For example, weight loss may occur during the time the samples are exposed to a very low humidity, when the water reservoir was low or if samples are weighed at the end of a drying cycle, when evaporation of moisture occurs. On the other hand, a weight increase would occur if samples are weighed at the end of a wetting cycle. Subsequently, moisture content in samples which is expected to vary through absorption or evaporation is determined gravimetrically. Assuming all processes would act equally on all samples by subtracting the weight change which affects the control sample from the weight change in the rest samples weight change from the treatments applied is obtained. The weight change in control samples due to moisture absorption/evaporation is therefore zero by definition.

Table 7.1 Salt up-take by sandstone after single immersion.

Sandstone type (n = 4)	Sodium sulphate up-take [g]	Sodium chloride up-take [g]
Locharbriggs	4.520±0.451	1.250±0.144
Crossland Hill	3.087±0.302	1.022±0.125



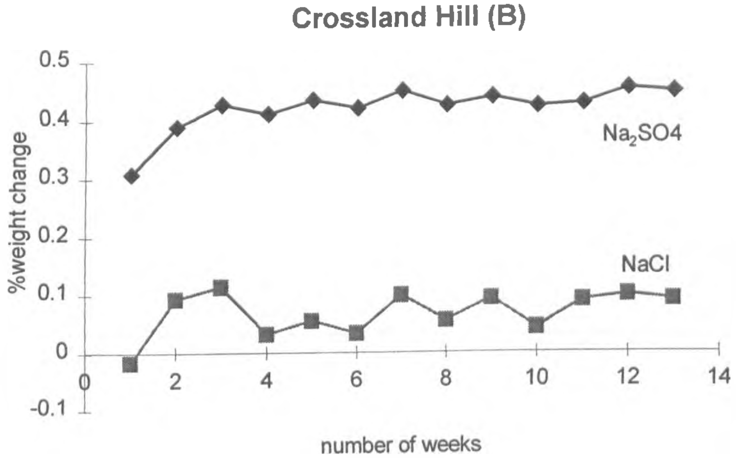


Figure 7.1a-b The mean percentage weight change with time for Locharbriggs after 50 cycles (A) and Crossland Hill after 80 cycles (B). Each cycle of 24 hours (12 hour of 5°C and 90 per cent humidity and 12 hour of 35°C and 70 % per cent humidity).

7.1.2 Porosity and pore size distribution

Results are reported on the porosity and pore size distribution changes after cyclical weathering of the salt-contaminated sandstone samples.

The Locharbriggs sandstone increased its overall porosity after cyclical weathering of both salt-contaminated samples (NaCl and Na_2SO_4). The Crossland Hill sandstone increased its porosity for the NaCl-contaminated sample but decreased for the Na_2SO_4-contaminated sample (Table 7.2). All results were compared to the initial porosity prior immersion and cyclical weathering.

Table 7.2 Porosities of sandstones after single immersion in salt solution and exposure to 50 cycles of humidity and temperature. Percentage change when compared to the initial porosity prior immersion.

Sandstone original porosity	Single immersion solution	Mean porosity, %	sd	Δporosity, %
Locharbriggs 18.23%	Water	21.55	0.43	3.32
	NaCl	25.29	0.38	7.06
	Na_2SO_4	23.97	0.65	5.74
Crossland 12.53%	Water	12.70	0.57	0.18
	NaCl	15.03	0.79	2.5
	Na_2SO_4	11.35	0.53	-1.18

Porosity was calculated by PoroSizer 9320 mercury porosimeter

Both sandstones were chemically cleaned prior to single immersion and cyclical exposure. The porosity at that point was 18.23% for Locharbriggs and 12.53% for Crossland Hill (Chapter 5). The behaviour and porosity changes after cyclical weathering are very different for the two sandstones. Locharbriggs sandstone overall porosity increased for all solutions included the control in deionised water. On the other hand, Crossland Hill sandstone overall porosity increased after immersion in NaCl and deionised water but decreased after immersion in Na_2SO_4. Dissolution and precipitation reactions could justify the increase and decrease in porosity.

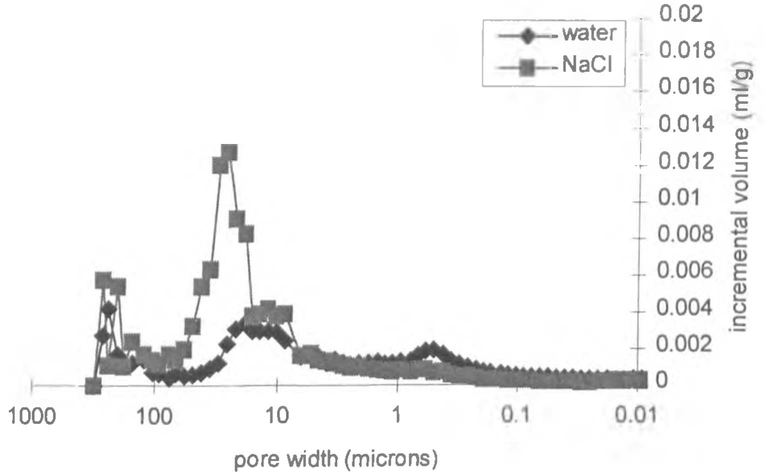
The differences in porosity distribution are well observed in the Locharbriggs samples (Figure 7.2 a-b). After cyclical exposure, samples immersed in both salt solutions showed a similar pattern in the distribution of porosity, especially the disappearance of microporosity between 0.5-1 μm compared to the control sample. The other characteristic porosity region for

Locharbriggs between 10-80 μm experienced similar distribution changes under NaCl and Na_2SO_4 solutions. In all cases, a shift towards the coarser region was accompanied by the creation of new porosity between 20-50 μm.

The development of porosity between 20-50 μm was also observed after partial immersion (Section 6.1) and one of the mechanisms proposed to explain the observed increase in porosity was the hydric dilatation and consequent change in the grain-to-grain distances. Similarly, hygric dilatation has also been observed during application of wetting/drying cycles of a NaCl-contaminated sandstone (Snethlage and Wendler, 1997). These authors reported that the grain-to-grain distances in salt-contaminated stones are smaller in the wet state (90% RH) than in the dry state (35% RH) and thus this contraction and expansion could explain the increase in porosity after cyclical weathering.

During the cyclical weathering study, dissolved salts will be transported and deposited periodically as moisture changes. If considering that the two salts had a tendency to filling the smallest pores of the stone then this will explain the reduction of porosity from the denominated microporosity region (pore width < 1 μm). This has been previously observed for NaCl (Rodriguez-Navarro and Doehne, 1998) in laboratory weathering studies and therefore confirm these findings.

(A)



(B)

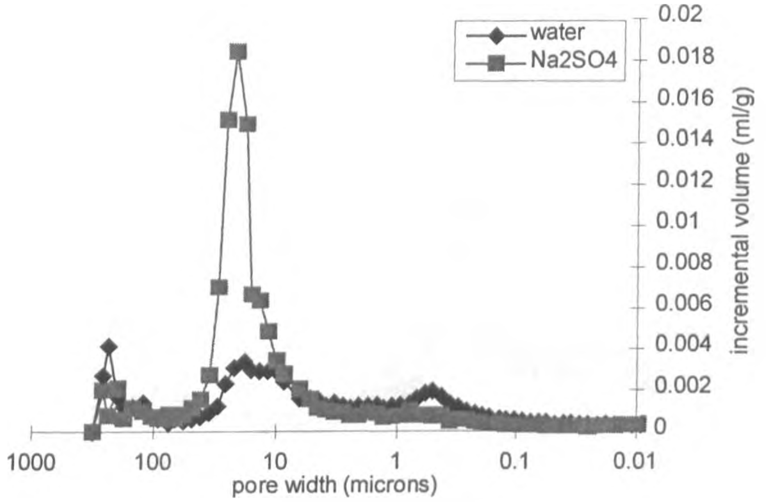
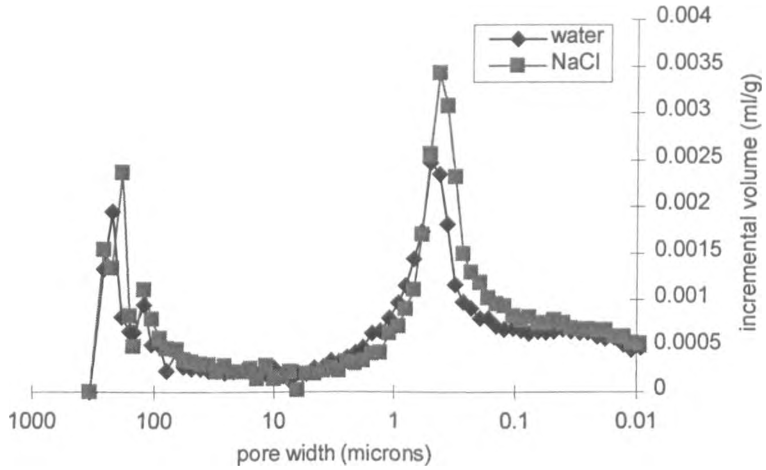


Figure 7.2 a-b Pore size distribution for the Locharbriggs samples after cyclical weathering for 50 cycles.

The porosity changes were not very significant for the Crossland Hill samples (Figure 7.3 a-b). The percentage porosity change when compared to the control in deionised water was between 1.3-2.3% and they concentrated on the coarser region between 100-500 μm. These results compare closely to the ones in Section 6.1 after partial immersion in salt solutions of NaCl and Na_2SO_4.

(A)



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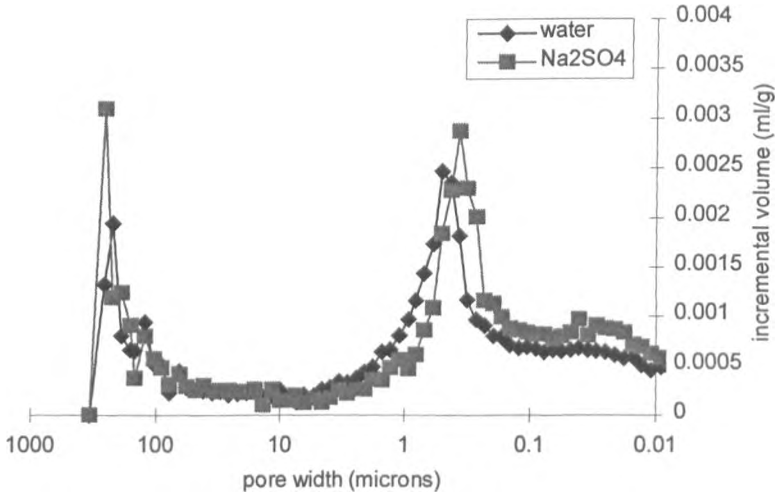


Figure 7.3 a-b Pore size distribution for the Crossland Hill samples after cyclical weathering for 50 cycles.

7.1.3 Scanning Electron Microscopy

This technique enabled examination of the surface of the stone at a very small scale and across areas of few microns (see section 3.4). Small samples of chemically cleaned sandstones were coated with a thin layer of Au/Pd prior to examination. Samples of Locharbriggs and Crossland Hill sandstone were observed after single immersion in deionised water, NaCl and Na_2SO_4 followed by cyclical weathering (section 7.1).

For the Locharbriggs sandstone, continuous cycling of cleaned control did not result in an obvious opening of the superficial porosity. Grains were not well observed (Plate 7.1a). Immersion in NaCl did not result in the appearance of salt crystals characteristic of sodium chloride although quartz grains appeared partly covered by a thin coating (Plate 7.1b). Immersion in Na_2SO_4 had a very similar effect on the appearance on the stone surface (Plate 7.1c). In both cases, grains were better observed than in the control sample and porosity seemed to open up.

For the Crossland Hill sandstone, the control sample in deionised water presented clean grain surfaces of the quartzs (Plate 7.2a). After immersion in NaCl (Plate 7.2b) and Na_2SO_4 (Plate 7.2c), more residual debris and smaller quartz grains were deposited on the surface and generally grains were not observed clearly.

Plate 7.1a-c SEM photomicrograph of the Locharbriggs cleaned surface after single immersion in deionised water (A), NaCl (B) and Na_2SO_4 (C) followed by cyclical weathering.

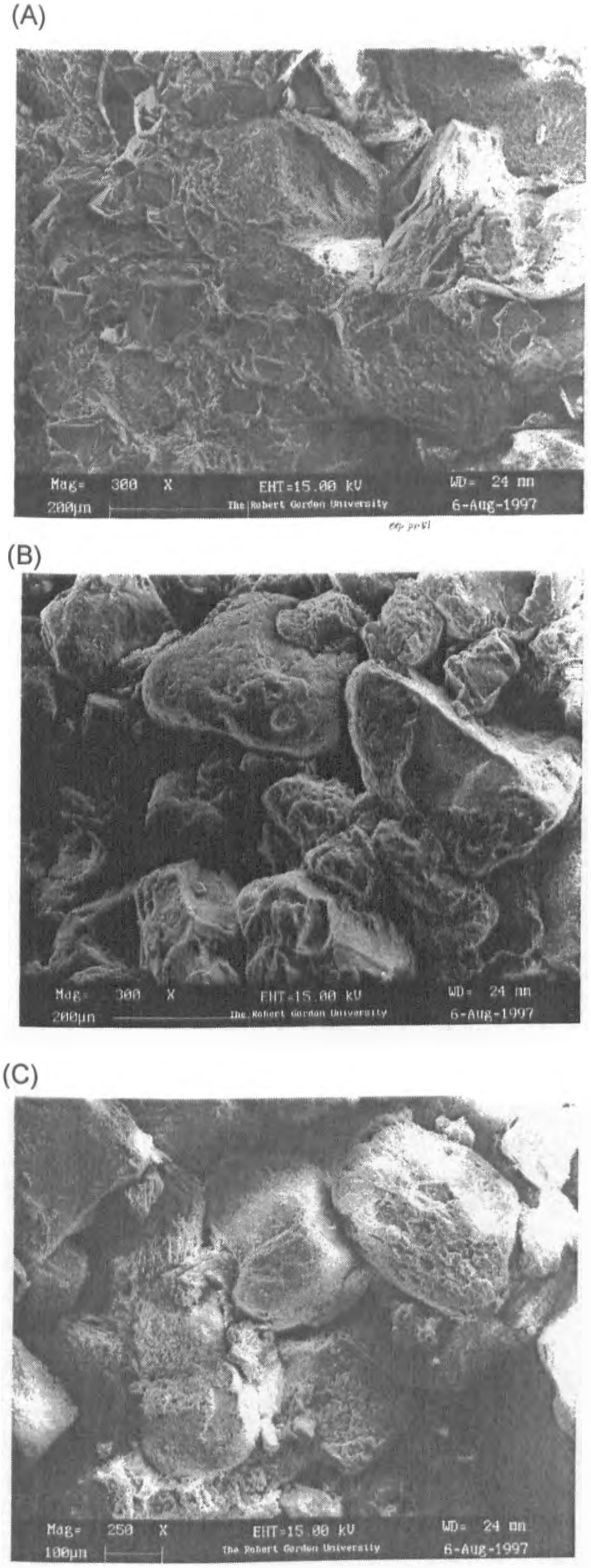
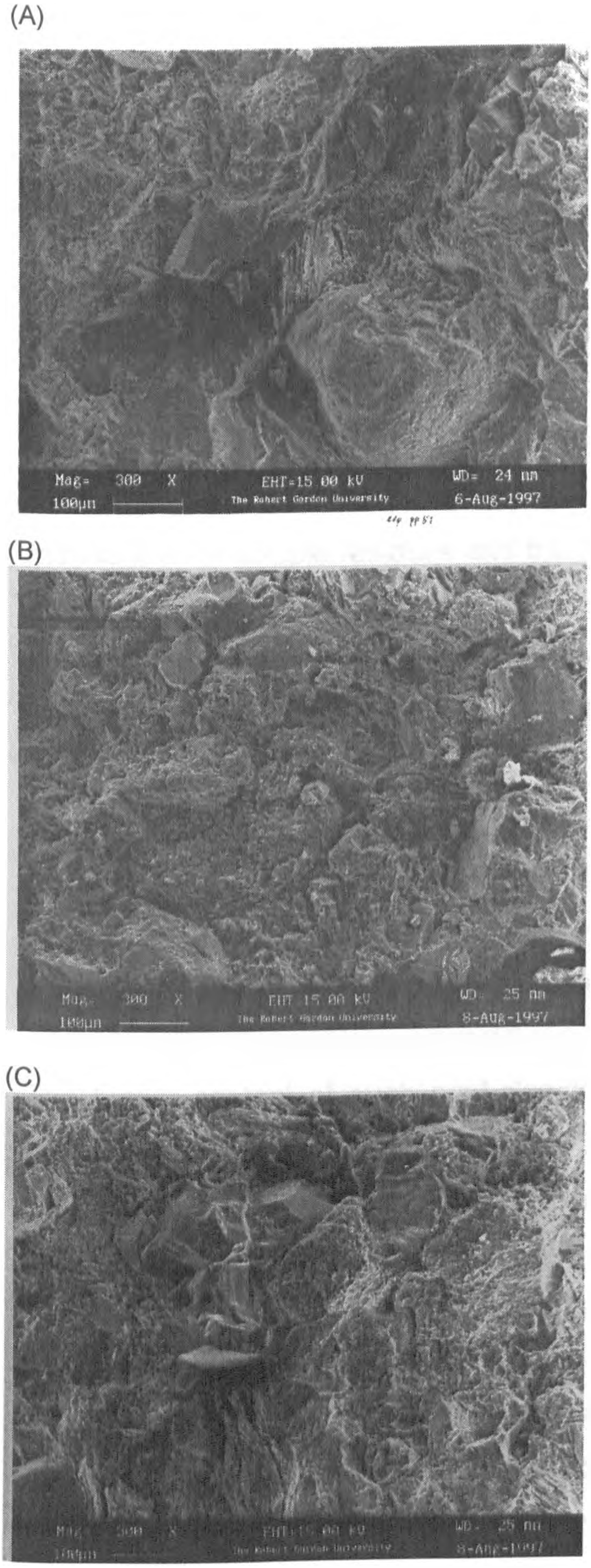


Plate 7.2a-c SEM photomicrograph of the Crossland Hill cleaned surface after single immersion in deionised water (A), NaCl (B) and Na_2SO_4 (C) followed by cyclical weathering.



7.1.4 Summary

Cyclical weathering of Locharbriggs and Crossland Hill sandstones after total immersion in NaCl and Na_2SO_4 resulted in very little damage. Relative weight changes indicated a very small variation with time.

Analysis of the porosity distribution of chemically cleaned sandstones after a single immersion in NaCl and Na_2SO_4 salt solutions and exposure to 50 (Locharbriggs) and 80 (Crossland Hill) RH/T cycles respectively indicated a change when compared to the control samples immersed in deionised water. For the Locharbriggs sandstone, these changes took place in a similar way for the two solutions studied (NaCl and Na_2SO_4) with development of new porosity in the region between 20-50 μm. These salts seemed to enhance the mobilisation of soluble residues and the dissolution reaction of clay fraction. For the Crosssland Hill sandstone, cyclical weathering did not have a significant effect on the porosity distribution. There was a slight increase in the pores ranged between 100-500 μm and a slight shift towards smaller porosity regions (0.1-1 μm).

The results agreed with the ones in chapter 6. Here as well, immersion in the control water followed by cyclical weathering also had an effect in porosity when compared to the initial porosity prior to immersion. The porosity increased a 3.32% for Locharbriggs and 0.18% for Crossland Hill. These changes imply a remobilisation of post-cleaning residues and other soluble ions within the stone. The higher content of such post-cleaning residues (Chapter 5) and clays in Locharbriggs compared to Crossland Hill together with an original higher porosity could explain the tendency for the first to undergo dissolution reactions unlike the Crossland type which is well cemented by quartz overgrowths and consequently more difficult to attack. The type of reaction expected in this case will be precipitation.

The two salts had a similar effect on the porosity distribution of Locharbriggs and Crossland Hill sandstones. Rodriguez-Navarro and Doehne (1998) reported differences in damage potential between sodium chloride and sodium sulphate and associated them to the differential crystallisation pattern and growth kinetics of the two salts as well as the solution physical properties (surface tension and evaporation rate). These potential differences did not result in a very significant change of porosity distribution for the sandstones studied. This could mean that changes in porosity are initially associated to physical and chemical processes such as dissolution and precipitation of soluble ions in the stone rather than crystallisation of salts.

Cyclical weathering resulted in the development of efflorescences on Locharbriggs samples. The Crossland sandstone did not develop any efflorescence for the same number of cycles.

SEM observations showed that the differences in porosity distribution reflect the differences in actual pore size. Actual pore sizes appear to lie mostly within the 50-100 µm diameter range. Crossland Hill, on the other hand, did not show a well developed system of pores.

7.2 Cycles of SO_2 exposure

The following two sections aimed at the understanding of the environmental factors (SO_2, pH, relative humidity, temperature) which promote the acceleration of salt formation which causes damage to stone or creates conditions under which stone decay occurs. In the first study, the effect of SO_2 gas on chemical (acid-based) cleaned sandstone surfaces (Section 7.2). In the second study (Section 7.3), chemical cleaned samples were artificially weathered in a temperature and humidity controlled chamber by using a water spray system adjusted to two different pH (pH = 4 and pH = 5.6).

The first study (SO_2 exposure) made use of an atmospheric corrosion chamber VSK300 in which chemically cleaned samples were exposed for 12 days to a constant flow of 10 ppm at 25°C and 80% relative humidity. Weight concentration of soluble ions and colour changes were monitored before and after the exposure period. The deposition products formed were examined by using scanning electron microscopy (SEM-EDX) coupled with elemental map analysis. Based on the results obtained by other researchers such as Mangio *et al.,* (1991), a model (single-cycle) was used to simulate the action of SO_2 on a surface of known characteristics.

7.2.1 Weight changes

Five samples of each sandstone type were used, one sample was only water washed and used as control while the other four were chemical cleaned. These samples (35 x 35 x 35 mm) were cut into two, so one half was exposed to SO_2 gas for 12 days and the other half was used as a reference control. The exposed samples were removed from the chamber once during the whole period of exposure in order to monitor any weight change (Table 7.3).

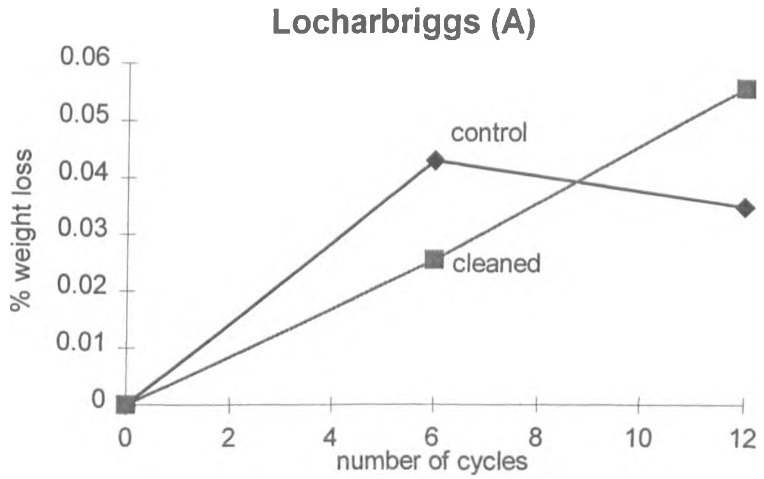
Table 7.3 Weight loss (%) after exposure to SO_2 for 12 days for the control and chemically cleaned sandstones (constant flow of 10 ppm at 25°C and 80% relative humidity).

Cycles/days	LOCHARBRIGGS		CROSSLAND HILL	
	Control	Cleaned (n = 4)	Control	Cleaned (n = 4)
6	0.043	0.03 ± 0.01	0.011	-0.02 ± 0.01
12	0.035	0.06± 0.01	0.08	0.08 ± 0.01
Total loss	*0.078*	*0.081±0.01*	*0.091*	*0.06 ±0.01*

$\%W=100(W_0 - W_1)/W_0$; where W_0 is the initial weight and W_1 is the weight at the end of the exposure.

The larger weight losses occurred after 12 cycles in the chamber. These weight losses which occurred due to exposure (constant flow of 10 ppm at 25°C and 80% relative humidity), indicated very small variation with time and this could be explained by the continuous precipitation and dissolution of the salts or by mechanical lost. In calcareous stones, such as limestone or calcareous sandstone, exposure to SO_2 would result in the expected increase in weight by formation of gypsum ($CaSO_4$) as reported in many studies (Mangio *et al.*, 1991). Silicate sandstones, such as the ones used in this study, are much more resistant and the changes in weight are probably associated to the loss of material (mechanical lost).

The percentage weight loss given in the figures (Figure 7.4a-b) are the averages values for two identical samples. The difference in weight loss between the two identical samples did not exceed the gravimetric accuracy. Upon the end of each exposure the samples were stored in a dessicator and weighed prior to examination under microscope (Section 7.2.3).



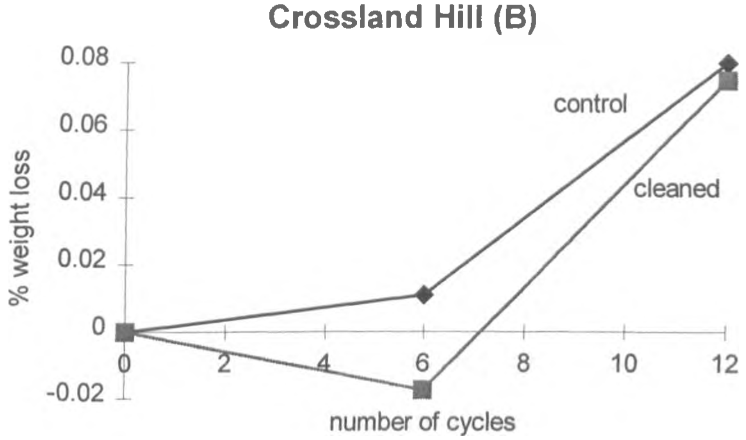


Figure 7.4a-b The values for weight changes (%) are the mean values (4 replicates ± sd) for the chemical cleaned samples after exposure to SO_2, 10 ppm. The values for the control were single values.

The total percentage weight change for both sandstone types was on average 0.06% for the chemical cleaned Crossland Hill and 0.09 % for the chemical cleaned Locharbriggs sandstone after exposure to SO_2, 10 ppm, with a trend to increasing in all cases. Any subtle action of this gas on the chemical cleaned surface of the sandstone can only be assessed by microscopy. Samples were first observed using light microscopy before further SEM analyses (Section 7.2.4).

7.2.2 Analysis of soluble residues

The analysis of soluble residues investigates the distribution of anions, sulphate in particular, after exposure in the atmospheric corrosion chamber VSK300. The average concentration values (n=3) for each of the ions (chloride, nitrate and sulphate) were taken at depths of 0-2, 2-5, 5-10 and 10-20 mm for the Locharbriggs and 0-2, 2-5 and 5-10 mm for Crossland Hill.

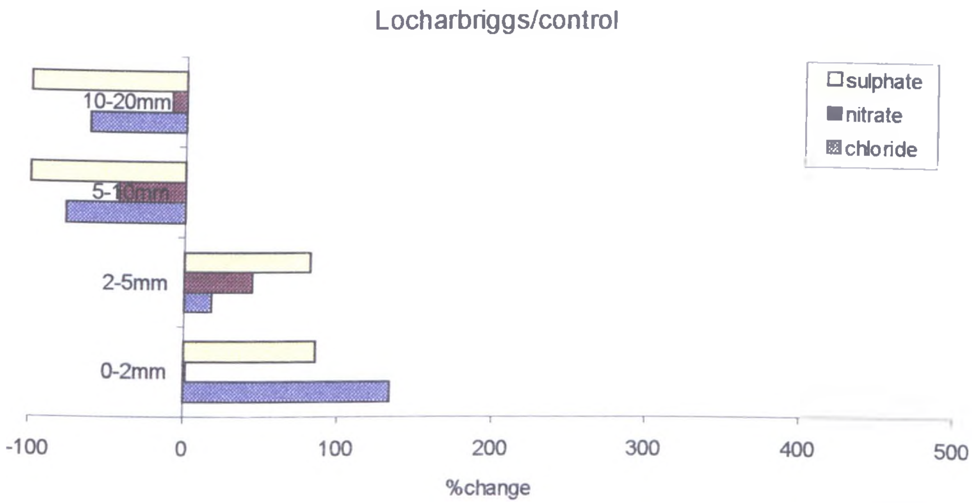
The percentage change on the concentration of soluble ions (chloride, nitrate and sulphate) before and after chemical cleaning was calculated at each depth, 0-2, 2-5, 5-10 and 10-20 mm.

Figures 7.5a-b show the results for Locharbriggs control and chemically cleaned samples. For the control samples, sulphate, chloride and nitrate, presented a similar trend: gain at the surface and loss after 5 mm depth. For the cleaned samples, sulphate levels increased for all depths, especially at the near-surface. Chloride and nitrate showed little change during the first 2mm then increased, especially chloride, from 2-5 mm, this was notably so for nitrate. The variations of these two anions compared to sulphate indicated that sulphate levels increased significantly during the cycles of weathering or in other words, exposure to SO_2 gas had an impact in the sulphate concentration of the chemically cleaned samples (Appendix 7.1).

The Crossland Hill samples followed a similar trend for control and chemically cleaned samples, showing an increase in sulphate levels at all depths (Figure 7.6a-b). For the control samples, the sulphate concentration increased almost 200% after exposure over the first 2mm and even at depths of 10mm, this change was over 100%. Chloride presented the same positive percentage change at all depths and nitrate only varied significantly between 2-5 mm. For the cleaned samples, sulphate concentrations were also higher at the near-surface (250%) than at depth. Chloride and nitrate either decreased or did not change after the experiment (Appendix 7.2).

Both control and cleaned samples increased their sulphate levels after artificial exposure to SO_2 gas but the cleaned samples showed a larger percentage change and this can be explained in terms of chemical composition. After cleaning, the stone surface is more alkaline in terms of sodium (from the cleaning agent), potassium and calcium (from the cleaning action) levels. It is known that SO_2 deposition rates are faster at the surface of materials of a calcareous nature because of their alkaline content (Mangio *et al.,* 1991). Here, the stone samples are not calcareous sandstones but the amount of sodium was increased after cleaning (see Chapter 5). Therefore, the SO_2 deposited on these surfaces will be readily oxidised to sulphate, which in the presence of calcium could combine to form gypsum.

(A)



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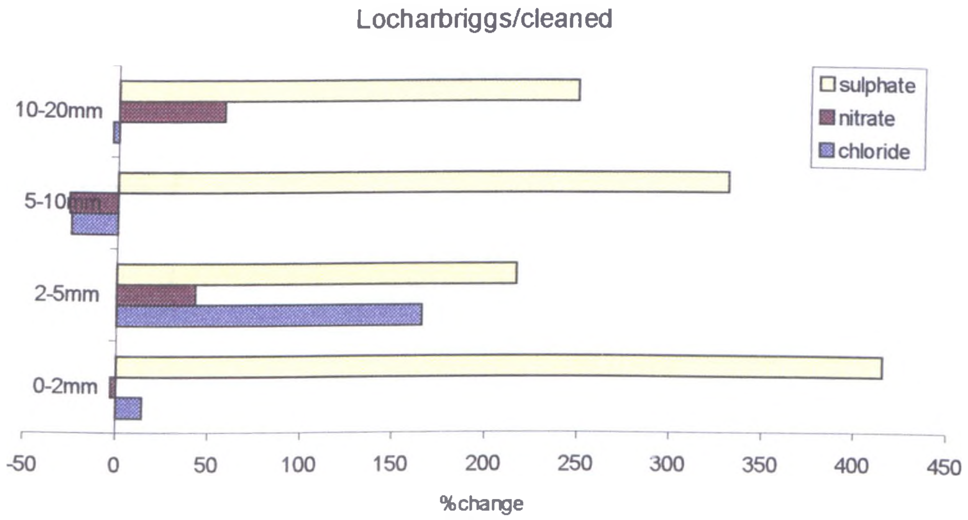


Figure 7.5 a-b The mean percentage changes for Locharbriggs sandstone after exposure to SO_2 for 12 days (constant flow of 10 ppm at 25°C and 80% relative humidity). Raw data in Appendix 7.1.

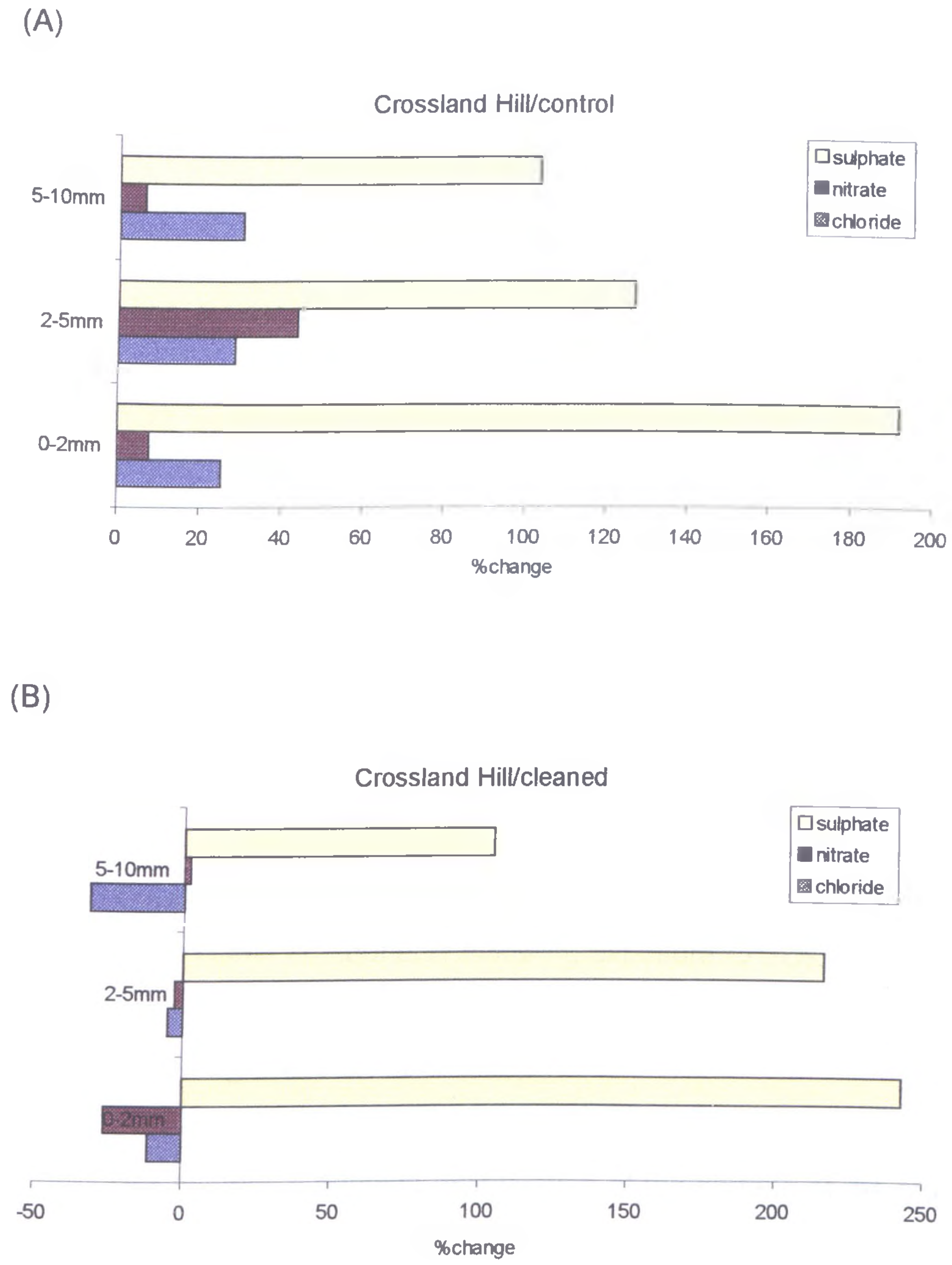


Figure 7.6a-b The mean percentage changes for Crossland Hill sandstone after exposure to SO_2 for 12 days (constant flow of 10 ppm at 25°C and 80% relative humidity). Raw data in Appendix 7.2.

7.2.3 Colour changes

The changes in colour components L* (brightness), a* (green to red) and b* (blue to yellow) as result of exposure to SO_2 were measured by using a Minolta Colour Meter CR-200b.

The average values (n=3) for the three components were compared before and after artificial exposure of the stone surfaces. The mean values and sd for both sandstones, Locharbriggs and Crossland Hill, are reported in Table 7.4.

Table 7.4 The mean and standard deviation values for L (brightness), a (green to red) and b (blue to yellow) both sandstones before and after SO_2 exposure.

CHANGES WITH ARTIFICIAL EXPOSURE							
Crossland Hill	L	a	b	**Locharbriggs**	L	a	b
Before exposure	61.32±1.68	1.58±0.13	16.97±1.22	Before exposure	49.8±3.27	12.11±1.32	15.65±1.30
After exposure	61.6±1.19	1.52±0.19	16.81±1.47	After exposure	48.32±2.41	11.62±1.85	15.76±1.52

These results indicate that there were not significant changes associated to any of the colour components following exposure to SO_2.

7.2.4 Scanning Electron Microscopy

This technique enabled examination of the surface of the stone at a very small scale and across areas of few microns (Section 3.4). Small samples of control and chemically cleaned sandstones were coated with a thin layer of Au/Pd prior to examination.

Additionally, elemental map analysis and EDX analysis were performed on some of the selected images to obtain further qualitative information on the main elements present on the surface selected. The ions selected and their colour on the photomicrographs shown were: sodium (green); magnesium (magenta); sulphur (cyan); chlorine (yellow); potassium (red); calcium (blue) and iron (orange).

After 12 cycles, neither series of samples showed any visible signs of deterioration.

Element map analysis of the Locharbriggs control sample indicated the presence of potassium, iron and localised deposits of calcium and sulphur. (Plate 7.3a). The soiling is extensive and there is probably some biological growth associated. Chemically cleaned samples presented a cleaner surface. After exposure to SO_2, some of the clay (smectite) seemed to disappear. This could be explained by the action of SO_2 which when oxidised to H_2SO_4 can dissolve some of this clay. An elemental map analysis of the surface revealed the presence of sulphur and calcium and therefore it could be concluded the composition as that of a polymorph, possibly gypsum (Plate 7.3b).

Analysis of the Crossland Hill control and cleaned samples by SEM indicated the presence of crystalline deposits on some feldspars and quartz grains. The analysis by element map showed the presence of sulphur and calcium deposits in both control (Plate 7.4a) and cleaned surfaces (Plate 7.4b). Also, potassium, sodium and iron were observed.

Plate 7.3a-b SEM photomicrograph and element map analysis of the Locharbriggs sandstone control (A) and cleaned surface (B) after exposure to SO_2 for 12 days. Colours correspond to the following ions: sodium (green); magnesium (magenta); sulphur (cyan); chlorine (yellow); potassium (red); calcium 9blue) and iron (orange).

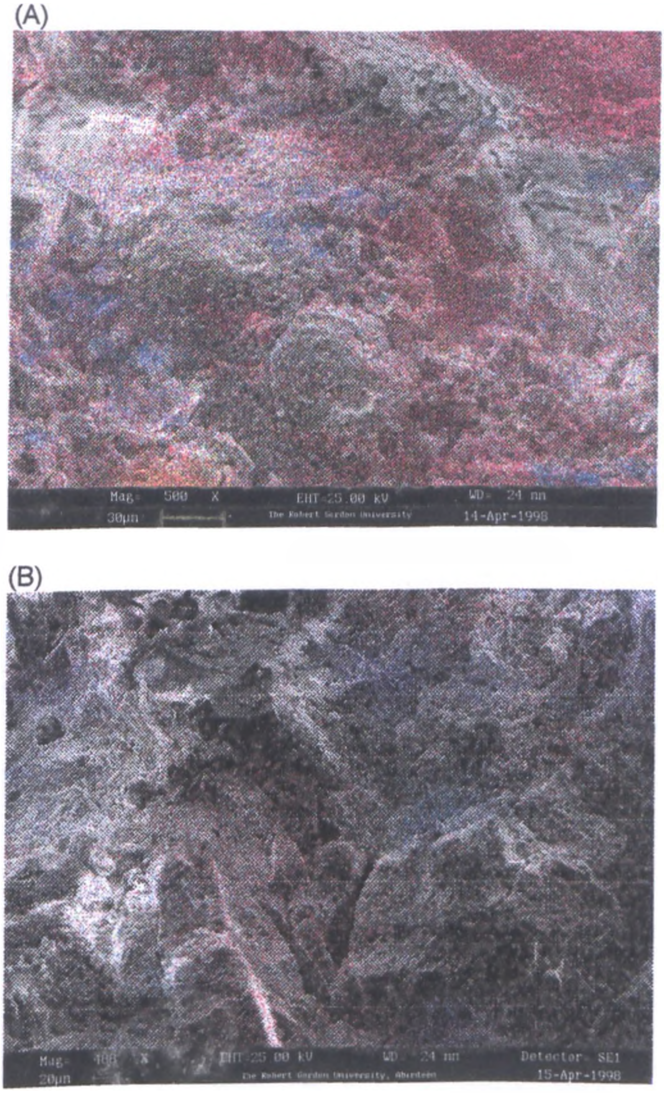
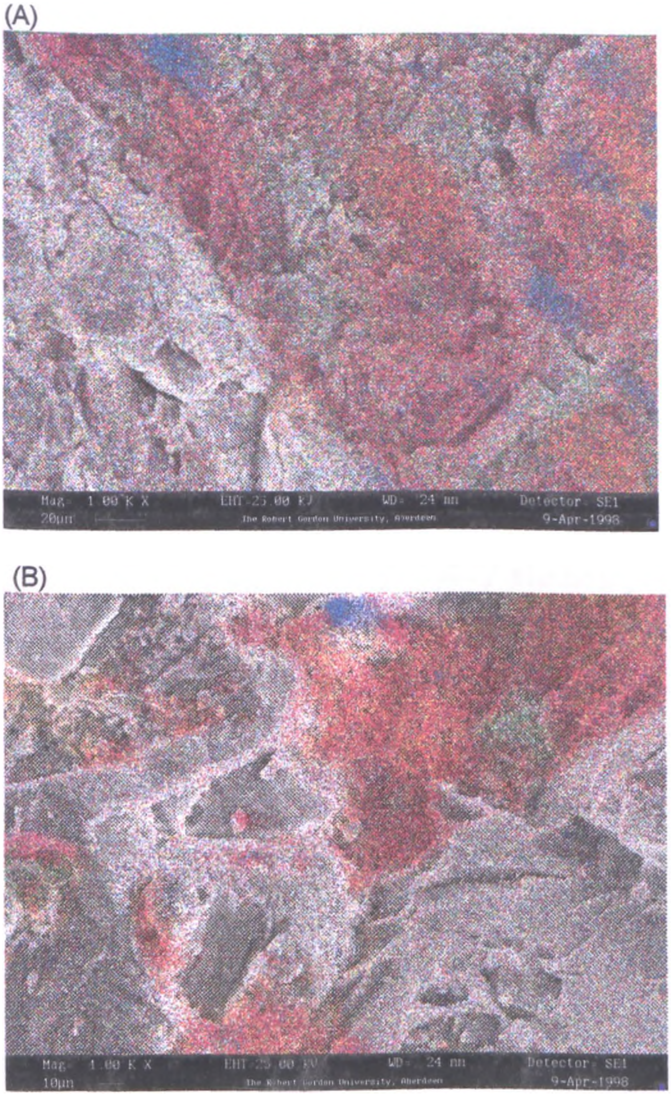


Plate 7.4a-b SEM photomicrograph and element map analysis of the Crossland Hill sandstone control (A) and cleaned surface (B) after exposure to SO_2 for 12 days. Colours correspond to the following ions: sodium (green); magnesium (magenta); sulphur (cyan); chlorine (yellow); potassium (red); calcium 9blue) and iron (orange).



7.2.5 Summary

The results for Lochabriggs and Crossland Hill (Figures 7.5a-b and 7.6a-b) showed that sulphate was introduced in the stone after exposure to SO_2 gas after 12 cycles up to depth levels of 20 mm. Chloride and nitrate ions were mobilised and their presence at different depths is probably a consequence of displacement reactions. Chemically cleaned samples presented the largest percentage changes at any depth. Therefore it can be concluded that exposure to SO_2 gas had an effect on the amount of sulphate found on the surface of Locharbriggs and Crossland Hill sandstones and that chemical cleaning favoured the conversion of SO_2 into H_2SO_4.

The mechanism of conversion of SO_2 into sulphurous and sulphuric acid has been reported in many studies (Winkler, 1994). The presence of catalytic oxidants, such as ozone and high RH accelerates the process (Mangio *et al.*, 1991). In this study, the build up of condensation on the stone surface favoured this process. Winkler (1994), further compared the differences in SO_2 levels between urban and rural areas and concluded that the sulphate attack on silicate stones, as the ones in our study, is not easily measured. Leaching of alkali metals and/or iron may take place. Appendix 7.4a-b, shows the results from the leaching studies on Locharbriggs and Crossland Hill cleaned sandstone. Exposure had an effect on the leachability of other solubles apart from sulphate which was expectedly leached in larger concentrations after exposure. For the Locharbriggs sandstone, the decreasing order of leached ions was: sulphate >>> sodium > potassium ~ magnesium. For the Crossland Hill, a similar trend was found: sulphate >>> sodium > magnesium > potassium.

This leaching would explain the results from the elemental map analysis which revealed the presence of sulphur and potassium deposits on the surface of the two sandstones. Sulphate is considered a powerful corrodent and the possibly reaction between mineral components and H_2SO_4 will lead to dissolution reactions of the feldspars, mica and clays and the leaching of potassium, sodium and magnesium (Section 1.4.2). These elements were found in large amounts together with sulphur at the surface of both sandstones.

The total percentage weight loss for both sandstone types was on average 0.06% for the chemical cleaned Crossland Hill and 0.09 % for the chemical cleaned Locharbriggs sandstone after exposure to SO_2, 10 ppm.

7.3 Influence of pH on cyclical weathering

In this experimental study, chemical cleaned Locharbriggs and Crossland Hill samples were cyclically weathered in a MPC/PB5 spray chamber, using a water spray at a pH representative of an urban area (pH 4) and that of a rural area (pH 5.6). The exposure period was carried out over four weeks for each pH. For the water spray at pH 4, a solution of H_2SO_4, 1% v/v concentration was used. Each cycle lasted for 24 hour with 12 hour of water spray and 12 hour of drying at a temperature of 40°C. For the control test, water spray at equilibrated pH 5.6 was used.

7.3.1 Weight changes

Three sandstone samples of each type were selected for the study, one sample was only water washed and used as control while the other two were chemical cleaned. The samples (exposed to a water spray system of pH 4 and pH 5.6) were removed from the chamber once (loss 1 after 12 cycles) during the whole period of exposure and at the end of the experiment (loss 2 after further 28 cycles) in order to monitor any weight change. The total weight loss given in Table 7.5 are the averages for two identical samples after a period of 40 cycles. The difference in weight loss between the two identical samples did not exceed the gravimetric accuracy.

Table 7.5 Weight loss (%) after exposure for 40 cycles for the control and chemically cleaned sandstones at pH 5.4 and pH 4.

pH 5.4	*LOCHARBRIGGS* *% weight loss*		*CROSSLAND HILL* *% weight loss*	
cycles	Control	Cleaned (n = 3)	Control	Cleaned (n = 3)
12	0.092	0.036±0.01	0.038	0.105±0.01
40	0.04	0.043±0.01	0.048	0.05±0.001
total loss	*0.132*	*0.079±0.01*	*0.086*	*0.155±0.01*

pH 4	*LOCHARBRIGGS* *% weight loss*		*CROSSLAND HILL* *% weight loss*	
cycles	Control	Cleaned (n = 3)	Control	Cleaned (n = 3)
12	0.080	0.077± 0.01	0.042	0.102±0.001
40	0.014	0.016± 0.01	0.019	0.025±0.001
total loss	*0.093*	*0.093± 0.01*	*0.061*	*0.128±0.01*

$\%W=100(W_0 - W_1)/W_0$; where W_0 is the initial weight and W_1 is the weight at the end of the exposure.

The effects of pH on the percentage weight loss were slightly different depending on the stone type and whether the stone was chemically cleaned or not. For example, the Locharbriggs control samples experienced a larger percentage weight loss at pH 5.5 compared to the cleaned samples and to the control Crossland Hill. The reverse applied to the Crossland Hill cleaned sandstones which underwent larger percentage weight losses than its equivalent control. Therefore at pH 5.5, chemically cleaned Crossland Hill samples were more affected than Locharbriggs.

The situation was quite similar at pH 4. In this case, the Locharbriggs samples experienced the same percentage weight loss regardless of the initial cleaning treatment. The percentage weight loss for the Crossland Hill cleaned samples was also larger than for the control sample.

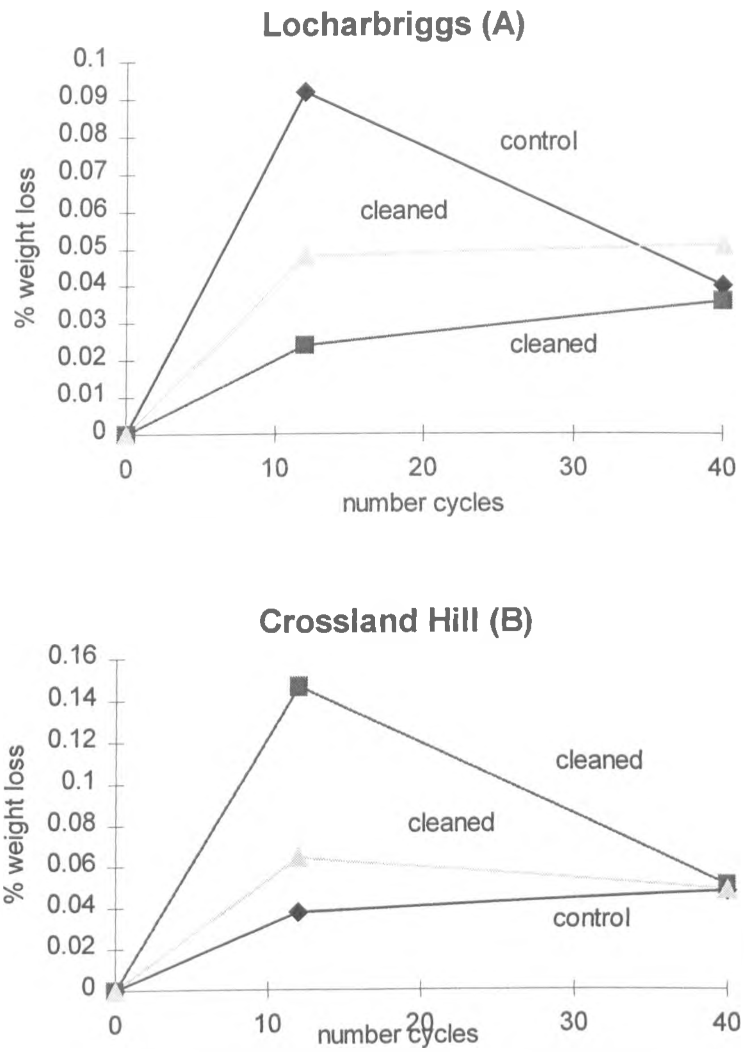
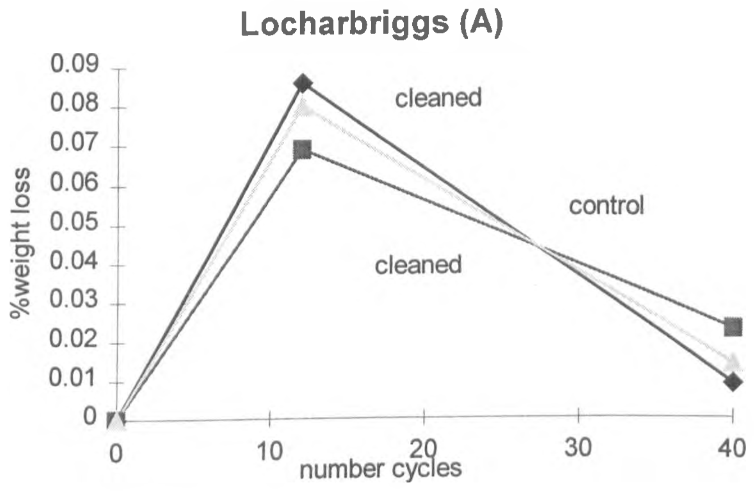


Figure 7.7a-b The values for weight changes (%) after exposure to a water spray system at pH5.6 for 40 cycles.



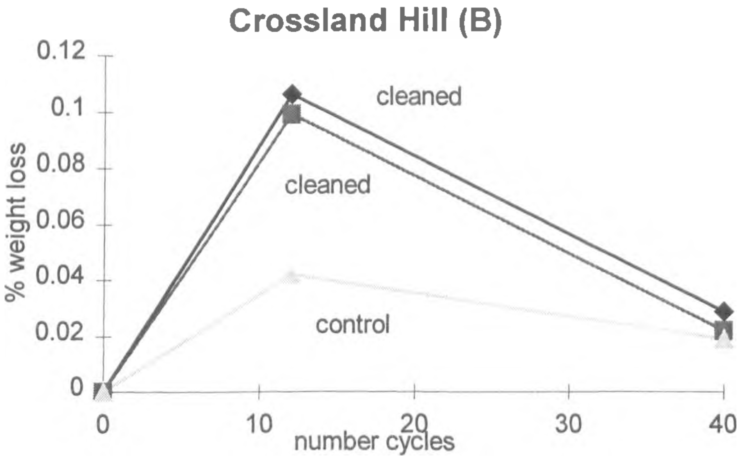


Figure 7.8a-b The values for weight changes (%) after exposure to a water spray system at pH 4.

The total percentage weight loss after 40 cycles was (0.09%) at pH 4 and (0.08%) at pH 5.6 for the Locharbriggs sandstone and 0.13% at pH 4 and 0.15% at pH 5.6 for the Crossland Hill sandstone (Table 7.4).

These weight changes, although small, indicated a trend in the global response of the stones to the cyclical weathering conditions used. These trends showed a peak for the percentage weight loss after 12 cycles. This loss did not increase after the samples were exposed for a further 28 cycles. This could be explained by the fact that cementing material was initially present at the stone surface and the physical and chemical action of the spray water initiated the material loss and consequent weight change. Once this first loss has occurred, further action of the spray water is reduced.

7.3.2 Summary

The results obtained indicated a weight loss after exposure to both pH water systems (pH 4 and pH 5.6) for the two sandstone types. The percentage weight loss was slightly different depending on the stone type and whether the stone was chemically cleaned or not. At both pH values, chemically cleaned Crossland Hill samples experienced a larger percentage weight loss than the control sample and the cleaned Locharbriggs.

The pH selected in these studies represented the typical pH for rain which is acid by nature (pH 5.6), and based only on the present equilibrium of the CO_2 content in the atmosphere with rainwater. To lower this pH by 0.2, Winkler (1994) reported the atmospheric CO_2 level should be doubled or tripled from 0.034 to 0.07%. The water spray solution at pH 4 was prepared by adding H_2SO_4 , 1% solution. These two pH intended to represent the pH of rainwater at a typical urban and rural location although as mentioned by Winkler, (1994) it is very difficult to measure rainwater pH as there are many variables to consider.

The weight loss observed in the experimental studies can be explained by the action of the water spray and the weathering of the mineral components in the sandstones.

Keller *et al.*, (1963) tried to quantify the weathering of silicate minerals by leaching common rock-forming silicates by both deionised and CO_2-charged water. The latter doubled the leaching rates for calcium, magnesium, sodium and potassium. Orthoclase feldspar and muscovite mica are much more sensitive to CO_2-charged waters than are other minerals. In similar studies by Aires-Barrios *et al.*, (1975) using deionised water, potassium was leached the most followed by sodium. Leaching in a 3.5% NaCl solution almost doubles the loss of ions. Appendixes 7.4a-b show the leaching trends for some soluble cations after immersion in deionised water for 20 days. In the Locharbriggs sandstone, sodium was leached the most followed by potassium and very little magnesium. For the Crossland Hill, sodium was also leached the most, then magnesium and potassium. These results do not agree with the reported by Aires-Barrios (1975) but then again, the samples were chemically cleaned and this is an additional factor influencing the leachability.

Crossland Hill sandstone has a significant content of orthoclase feldspar and mica compared to Locharbriggs. The possibility of dissolution reaction of these aluminosilicates would result in the release of silica, aluminium, potassium and magnesium cations. On the other hand, Locharbriggs has more clay and dissolution of these clays would explain the leaching of potassium and magnesium in this sandstone. The large leaching of sodium for both sandstones can be explained by the presence of post-cleaning residues and also by the leaching of feldspars. These products of reaction if deposit as non-crystalline aluminium and silicon forms can probably contribute to a reduction of pore space. There are evidences to suggest these type of precipitation reactions will take place in acidic conditions (Wilson, 1987).

7.4 Conclusions

Cyclical weathering studies carried out on chemical cleaned samples have not been reported previously, and therefore represented a novel use of the temperature and humidity controlled chambers.

Cyclical weathering of Locharbriggs and Crossland Hill sandstones after total immersion in NaCl and Na_2SO_4 resulted in very little damage. The changes in porosity distribution caused by two different NaCl and Na_2SO_4 were very similar for each sandstone. The overall porosity increased in Locharbriggs after immersion and cycling and these changes were similar to the ones observed after partial immersion (see Chapter 6). Crossland Hill overall porosity did not change very significantly after immersion and cycling. These results also compared to the small changes in porosity after partial immersion without cycling.

Accelerated ageing of the stone was induced under controlled conditions (SO_2, pH, relative humidity and temperature). After exposure to SO_2, 10 ppm, the weight loss and colour changes for both sandstone types was not very significant. The oxidation of SO_2 and transformation into H_2SO_4 took place after exposure. Chemical cleaning increased the concentration of sulphate found in both sandstones when compared to the control samples, especially at the near-surface. These levels increased by a factor of 5 in the Locharbriggs and by a factor of 0.5 in the Crossland Hill (Appendixes 7.1 and 7.2). After cyclical weathering of samples at acid pH, the percentage weight loss was very small. The Crossland Hill cleaned samples experienced the largest weight loss (0.15-0.12%) and this was explained in terms of different mineralogy.

For a country such as UK, where the pH of the rain range between 4-6.5 (UKRGAR, 1990) these results could translate into the following conclusions: sandstones of a particular mineralogy will be more prone to dissolution reactions and adsorption of atmospheric pollutants and therefore will readily weather when placed at particular environments.

8 FIELD STUDIES: The influence of geographical location on porosity, mobile ions and colour

In previous chapters, the study of the processes and effects associated to salt-induced weathering of sandstones involved the use of laboratory controlled conditions. The salt weathering studies involved the partial immersion in saline solutions at constant temperature and humidity (Chapter 6). The cycling weathering studies reproduced the conditions of a typical Scottish mild summer, with cycles of humidity and temperature on salt-contaminated sandstones (Chapter 7). The effects of pollution and acid rain were also studied in cycling weathering studies involving the exposure of sandstone samples to SO_2 and acid pH (Chapter 7). Now, this chapter describes the results found after natural exposure of the Locharbriggs and Crossland Hill samples. The possibility of environmental/climatic influence on the action of salts in cleaned sandstone (drying/wetting cycles, salt crystallisation and salt migration) was investigated by exposing Locharbriggs and Crossland Hill sandstones to four different locations around Scotland (Banff, rural-coastal; Dunkeld, rural-inland; Aberdeen, urban-coastal and Glasgow, urban-inland).

8.1 Porosity and pore distribution

The results for overall porosity of the control and chemically cleaned samples are summarised in Table 8.1. The percentage porosity change after exposure for 24 months in Aberdeen (urban-coastal), Glasgow (urban-inland), Banff, (rural-coastal) and Dunkeld (rural-inland) are reported in Table 8.2.

The differences between the control and the cleaned samples were discussed in chapter 5.1.

The results from Tables 8.1 and Table 8.2 indicate there was a reduction in the overall porosity for Locharbriggs samples at all field sites, with the exception of Banff where the control sample increased its porosity 1%. The order of decrease in porosity percentage as a function of location for the cleaned samples was: Banff>Dunkeld>Glasgow>Aberdeen.

A comparison of overall porosity for the Crossland Hill samples before (t=0) and after (t=24 months) exposure indicated a significant reduction in porosity for the cleaned samples and only a very small variation for the control samples. The reduction order as a function of location for the cleaned samples was: Dunkeld>Aberdeen>Glasgow>Banff (Table 8.2).

Table 8.1 Porosities of sandstones after field exposure for 24 months.

Sandstone	Field site[1]	Control		Chemically cleaned	
		Porosity, %	sd	Porosity, %	sd
Locharbriggs	Before exposure	22.41	0.12	18.23	0.14
	Aberdeen (UC)	17	0.43	18.04	0.34
	Glasgow (UI)	16.70	0.32	16.32	0.40
	Banff (RC)	23.50	0.71	14.85	0.65
	Dunkeld (RI)	13.68	0.80	15.44	0.78
Crossland	Before exposure	9.75	0.30	12.53	0.42
	Aberdeen (UC)	10.23	0.34	8.71	0.72
	Glasgow (UI)	9.85	0.67	9.23	0.54
	Banff (RC)	9.10	0.46	11.33	0.43
	Dunkeld (RI)	10.35	0.62	6.78	0.50

[1] urban-coastal (UC); urban-inland (UI); rural-coastal (RC) and rural inland (RI).

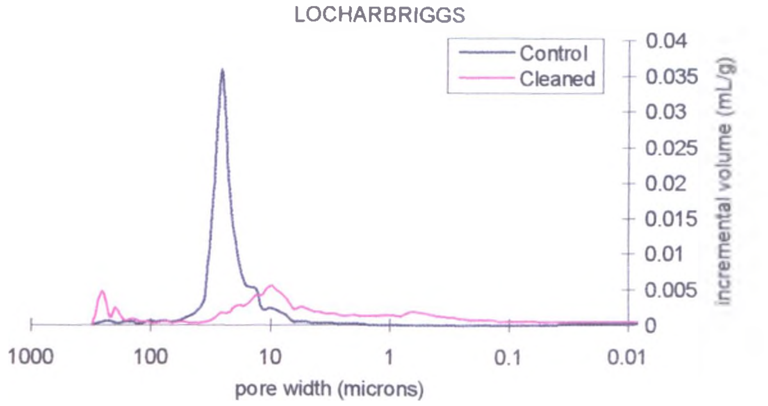
Table 8.2 Percentage porosity change after field exposure for 24 months.

Field site	Locharbriggs, Δporosity, %		Crossland-Hill, Δporosity, %	
	Control	Cleaned	Control	Cleaned
Aberdeen (UC)	-5.41	-0.19	0.48	-3.79
Glasgow (UI)	-6.71	-1.91	0.10	-3.30
Banff (RC)	1.09	-3.38	-0.65	-1.20
Dunkeld (RI)	-8.73	-2.79	0.60	-5.75

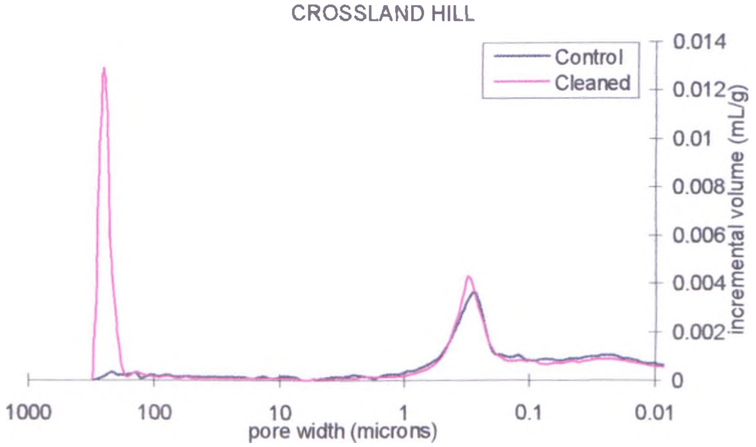
From these results it can be concluded that environmental exposure had a similar overall effect on both sandstones, normally a reduction in porosity. The differences laid on the influence of the location in that reduction. For example, both the Locharbriggs control and the Crossland Hill cleaned samples suffered the largest percentage change in porosity, especially after exposure in Dunkeld. This can be explained in terms of initial porosity. The initial porosity was larger in the control Locharbriggs and also in the cleaned Crossland Hill (Table 8.1). When exposed, these stones are more likely to absorpt and retain more water in the pore network and therefore more possibilities for dissolution and displacement reactions to take place. Further deposition of these soluble ions as secondary salts will explain the reduction in porosity (Camuffo, 1995).

The pore size distribution will be discussed individually for each site and also compared to the initial porosity before exposure. The porosity distribution for Locharbriggs and Crossland Hill sandstones before exposure (t=0) is shown in Figure 8.1a-b.

(A)



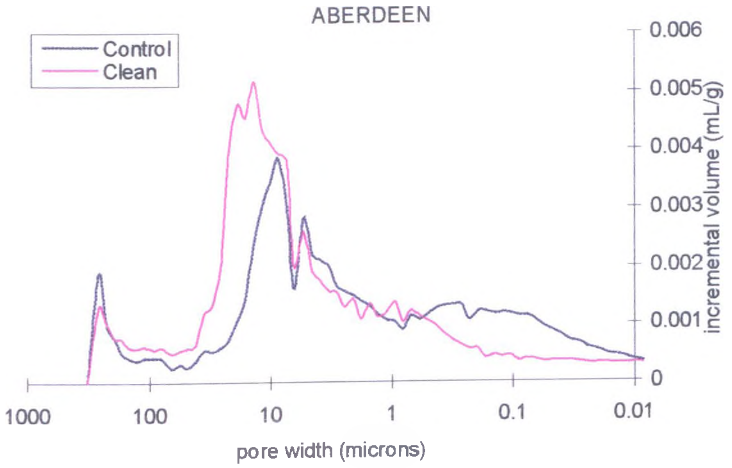
(B)



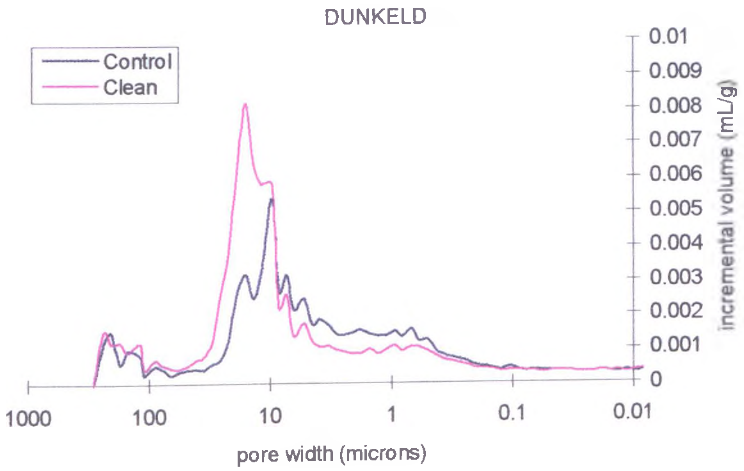
Figures 8.1a-b Pore size distribution for Locharbriggs (A) and Crossland Hill (B) control and chemically cleaned samples before exposure (t=0).

The changes in the pore size distribution for the control and cleaned Locharbriggs samples exposed in Aberdeen and Dunkeld were similar, with a widening and increase in the pores ranged between 10-70 μm (Figures 8.2a-b). For Glasgow, no differences were observed between the control and cleaned samples (Figure 8.2c). The major changes occurred in Banff, with the almost disappearance of porosity between 20-70 μm for the cleaned sample (Figure 8.2d). There were not significant changes in the porosity distribution of the control sample.

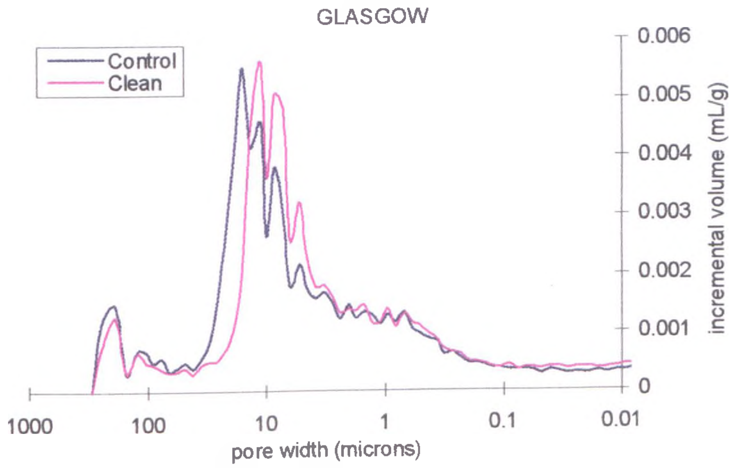
(A)


ABERDEEN
Control
Clean
0.006
0.005
0.004
0.003
0.002
0.001
0
incremental volume (mL/g)
1000
100
10
1
0.1
0.01
pore width (microns)

(B)


DUNKELD
Control
Clean
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
incremental volume (mL/g)
1000
100
10
1
0.1
0.01
pore width (microns)

(C)


GLASGOW
Control
Clean
0.006
0.005
0.004
0.003
0.002
0.001
0
incremental volume (mL/g)
1000
100
10
1
0.1
0.01
pore width (microns)

(D)

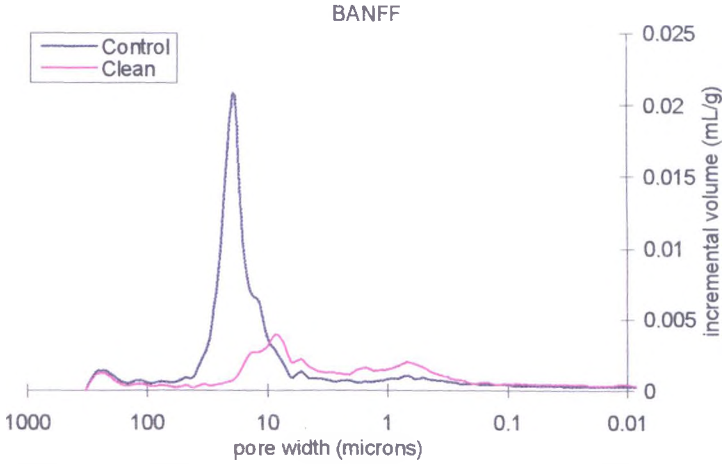
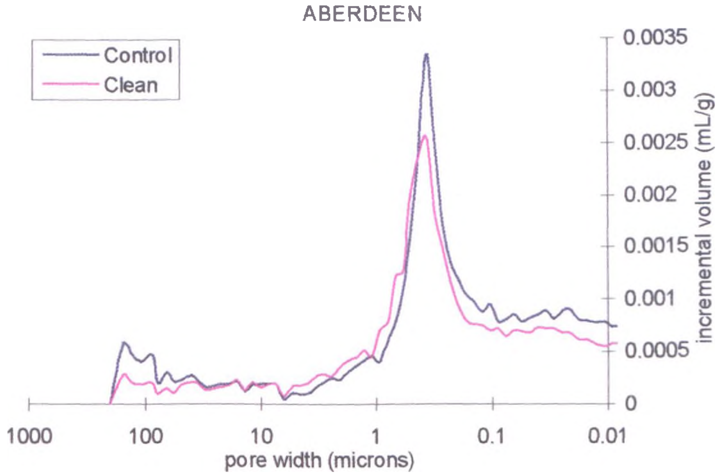
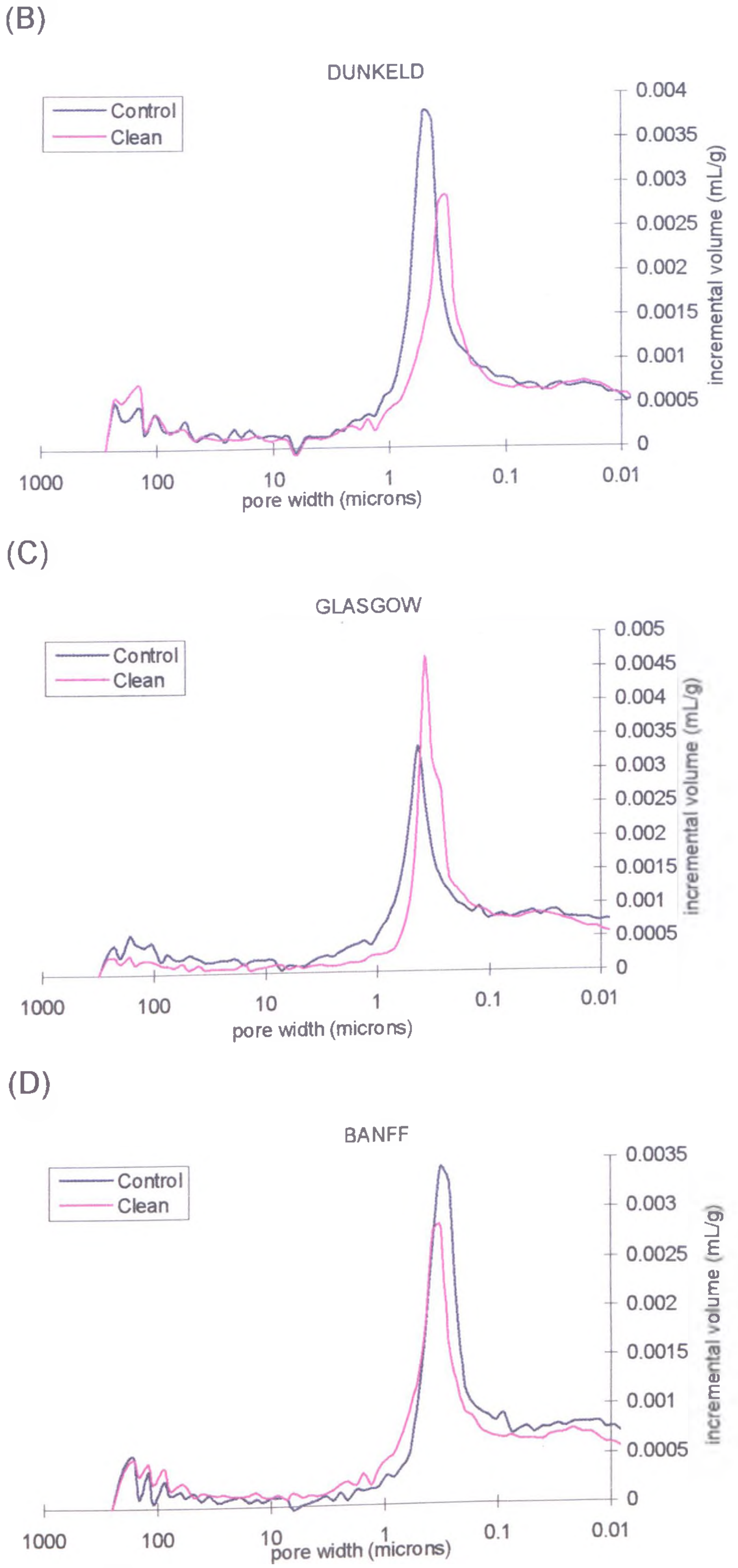


Figure 8.2a-d Pore size distribution for Locharbriggs samples after field exposure for 24 months.

Similar patterns were observed for the control and cleaned Crossland Hill samples with a decrease in the porosity region between 0.01-1 μm for the cleaned samples at all field sites (Figures 8.3a-c).

(A)



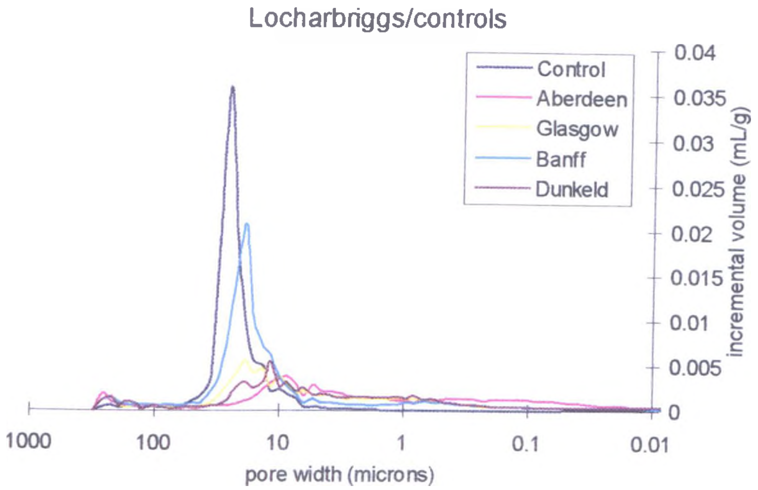


Figures 8.3 a-d Pore size distribution for Crossland Hill samples after field exposure for 24 months.

The Locharbriggs control samples experienced a decrease in overall porosity after the two-year exposure period in all field sites. The loss of porosity was mainly observed at the pore range between 10-80 µm, especially for the samples exposed in Glasgow and Aberdeen (Figure 8.4a). When observing the porosity distribution for the chemically cleaned samples for the same period of time (Figure 8.4b), a decrease in the macroporosity (200-500 µm) was observed in all field sites.

The Crossland Hill control samples presented a similar porosity distribution before and after field exposure (Figure 8.5a). Only the microporosity (<0.1 µm) decreased with time, especially at Dunkeld. The chemically cleaned samples varied in their porosity distribution with field site, for example all sites but Glasgow presented a redistribution in microporosity in the region between 0.2-1.0 µm (Figure 8.5b).

(A)



(B)

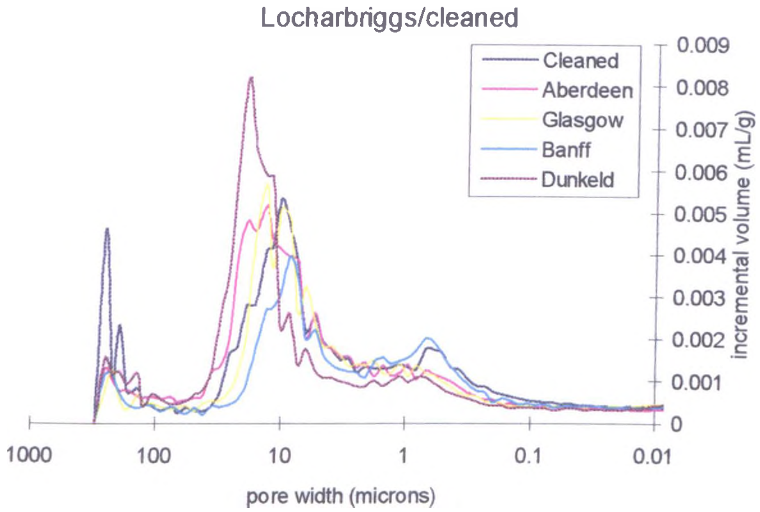
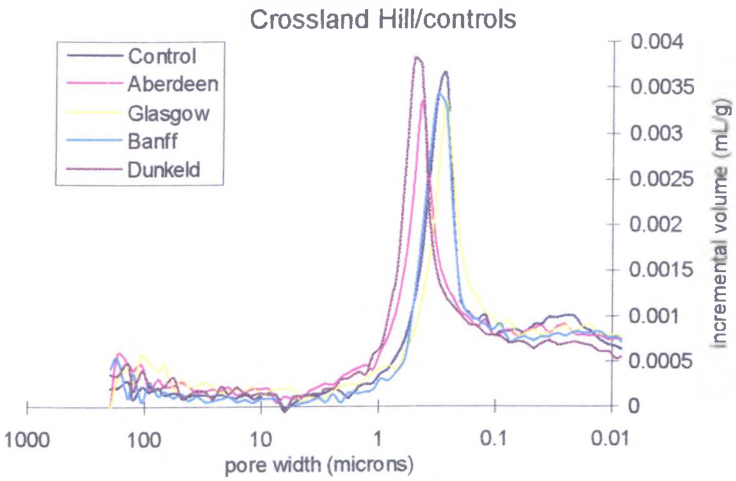


Figure 8.4a-b Pore size distribution for the Locharbriggs control (A) and cleaned (B) samples before (t=0) and after exposure for 24 months. Decrease in porosity after exposure can be observed.

(A)



(B)

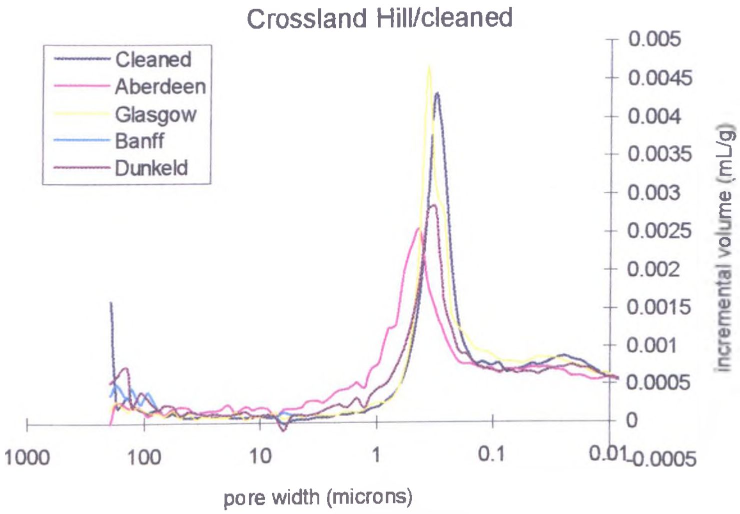


Figure 8.5a-b Pore size distribution for the Crossland Hill control (A) and cleaned (B) samples before (t=0) and after exposure for 24 months. Decrease in porosity after exposure can be observed for the cleaned samples.

8.1.1 Summary

Exposure of the Locharbriggs sandstone samples for 24 months had an effect on overall porosity. Although this effect was a net reduction of porosity for both controls and cleaned samples, it was found that the percentage change was, in general, larger for the control samples. This means that these samples were more affected by the exposure period than the cleaned samples. The porosity changes were concentrated in the pore size between 10-80 µm. Therefore any deposition of secondary salts from within the stone (weathering of minerals) or from external sources (deposition of pollutants or marine salt aerosol) occurred at this level.

Exposure of Crossland Hill samples for 24 months resulted in either a reduction in porosity (cleaned samples) or no significant change (control samples). The porosity loss can be explained by the dissolution and precipitation reactions within the stone and the adsorption of gases and salts from external sources.

8.2 Investigation of soluble salts after depth profiling

8.2.1 Analysis of soluble ions

The ions selected for chemical analysis (sodium, potassium, magnesium, sulphate, nitrate, chloride and fluoride) represent the main indicators of which type of decay process, associated to soluble salts, has taken place. The design of the experiment involved selection of a standard protocol described in Section 3.4.

The results for the concentration of the soluble ions (sodium, potassium, magnesium, sulphate, nitrate, chloride and fluoride) before and after exposure were compared for the control and chemically cleaned samples. This was done by calculating the percentage change as the difference between the average values (n=2) for the soluble ions before and after exposure at depth zones of 0-2, 2-5, 5-10 and 10-20 mm for the Locharbriggs and 0-2, 2-5 and 5-10 mm for

Crossland Hill. The mean values and standard deviation were further used for the statistical treatment of the results.

The percentage concentration change of the soluble ions (sodium, potassium, magnesium, sulphate, nitrate, chloride and fluoride) before and after exposure at the four field sites selected (Glasgow, Aberdeen, Banff and Dunkeld) was calculated at each of the following depths, 0-2, 2-5, 5-10 and 10-20 mm.

The analysis of the Locharbriggs control samples (Figure 8.6a) showed no significant change in ion behaviour with location for sodium, chloride and sulphate and in all cases, there was a loss in concentration after exposure. Nitrate changes were only significant in Aberdeen with almost a 40% increase, probably associated to atmospheric pollution (Section 3.7). The percentage change for fluoride was clearly dependent on location. Samples exposed at rural locations had the largest negative percentage change and therefore loss with exposure while samples located at urban locations, especially in Aberdeen, did not significantly change its fluoride levels. Potassium was also clearly influenced by the location with the major loss at Banff. The results for both ions could be explained if Banff is considered as the most exposed site of all and therefore with more opportunities for aggressive climatological conditions to exert a weathering action on the stone minerals with consequent leaching of potassium from the clays and fluoride from the muscovite mica.

The analysis of percentage change with depth (Figure 8.6b) showed how chloride was mainly leached out from the near-surface zone. The remainder of the ions decreased in concentration throughout the entire depth profile. This means exposure had a significant weathering effect not only at the near-surface but throughout the 20mm depth and the net effect was reduction in the concentration of the soluble ions considered in the study.

The effect of location on the percentage change of ions in the Locharbriggs cleaned samples (Figure 8.7a) showed no significant differences for the distribution pattern of sulphate, sodium, fluoride and potassium. There was a decrease in the concentration of these ions for all field sites. The percentage change of chloride with location was particularly significant. Chloride levels increased at the coastal sites (Aberdeen and Banff) and decreased at the inland sites (Glasgow and Dunkeld). Nitrate only increased in Aberdeen and decreased significantly for the other three locations.

The analysis of percentage change at each depth (Figure 8.7b) showed a comparable effect for all ions but chloride, reduction in the concentrations levels (Figure 8.7b).

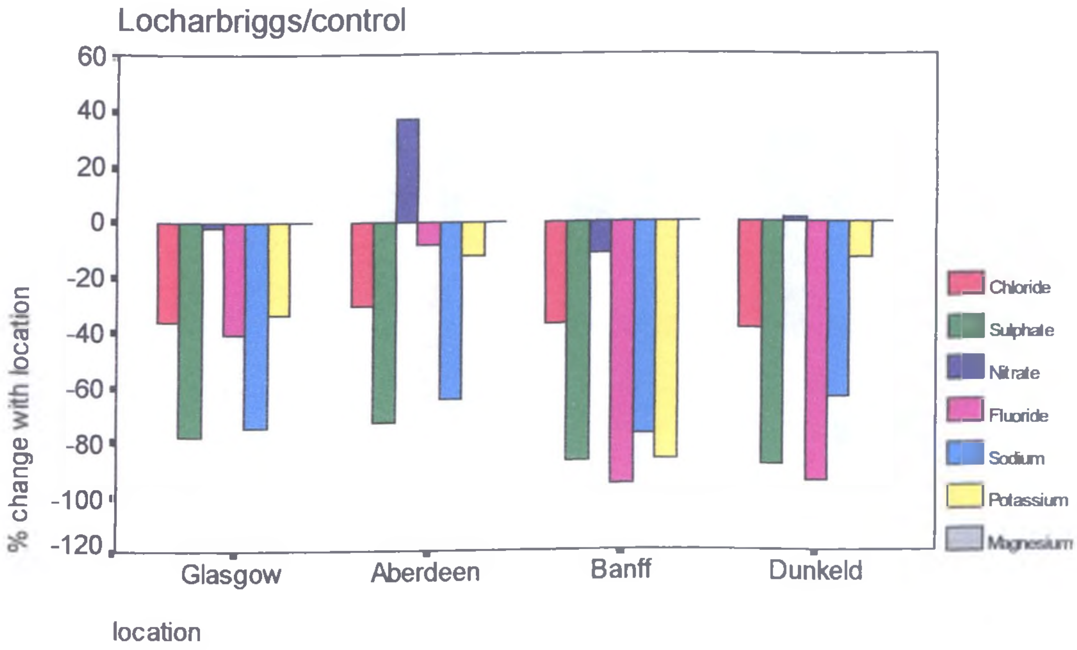
For the Crossland Hill control (Figure 8.8a), location had a significant effect in the distribution of magnesium concentration, especially at rural sites. This is probably related to the weathering of biotite mica which would release magnesium and potassium ions within the stone matrix and further precipitate salts such as KF (solubility, 49.6 g/100g) (Section 4.4). There were also some significant differences between the percentage change of chloride and sulphate at urban and rural sites. In all cases but magnesium, a reduction in the concentration of the ions was observed.

The percentage change variation at each depth was only significant for nitrate and sulphate. The concentration of these ions decreased preferentially at the near-surface. The remainder of the ions decreased similarly at each depth (Figure 8.8b).

The effects of location on Crossland Hill chemically cleaned samples (Figures 8.9a) were significant for magnesium and nitrate. Again the samples exposed at the rural sites gave a larger positive percentage change for magnesium, whereas the reduction in the concentration of sulphate and nitrate was more important at the urban sites (Glasgow and Aberdeen). Potassium loss was greater at coastal sites (Aberdeen and Banff). This can also be explained considering the weathering of micas and feldspar and the leaching of magnesium and potassium within or out of the stone matrix.

The average percentage changes at each depth only showed significant differences for nitrate (Figure 8.9b) with concentrations declining with depth. A pattern showed by both, control and cleaned samples.

(A)



(B)

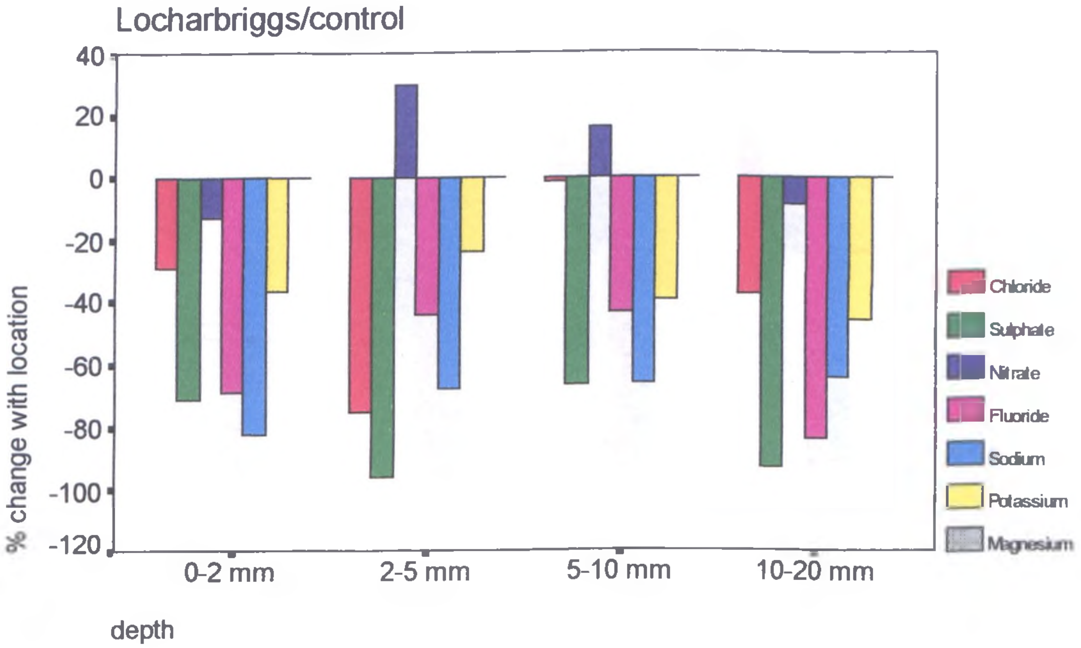


Figure 8.6a-b The percentage concentration change of the soluble ions before and after field exposure was calculated at each location (A) and the average at the four locations at depths 0-2, 2-5, 5-10 and 10-20 mm (B). Mean concentration before cleaning was subtracted from the mean concentration after cleaning and divided by the initial value: $(C_1 - C_0)/C_1*100$. Raw data in appendix 8.1.

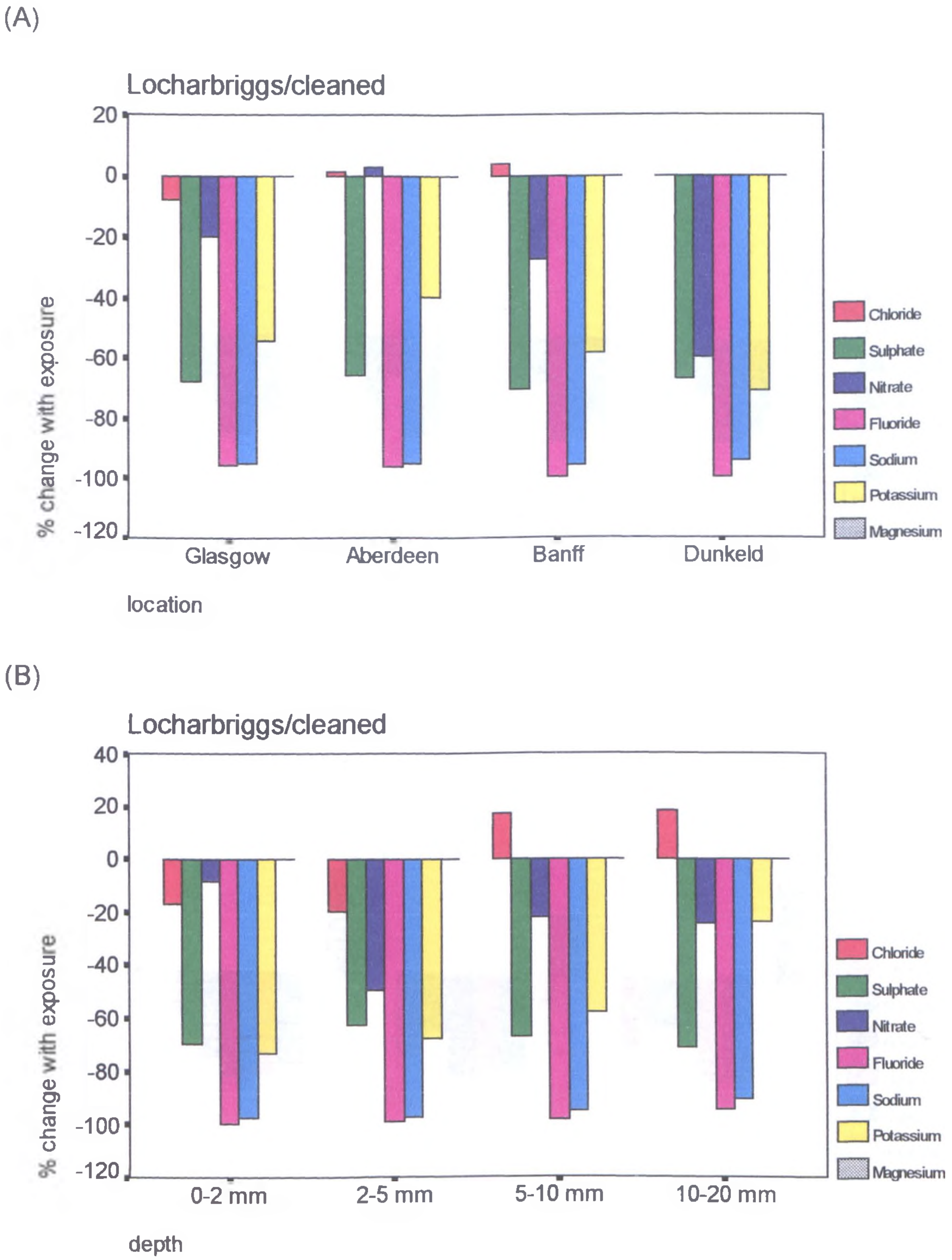
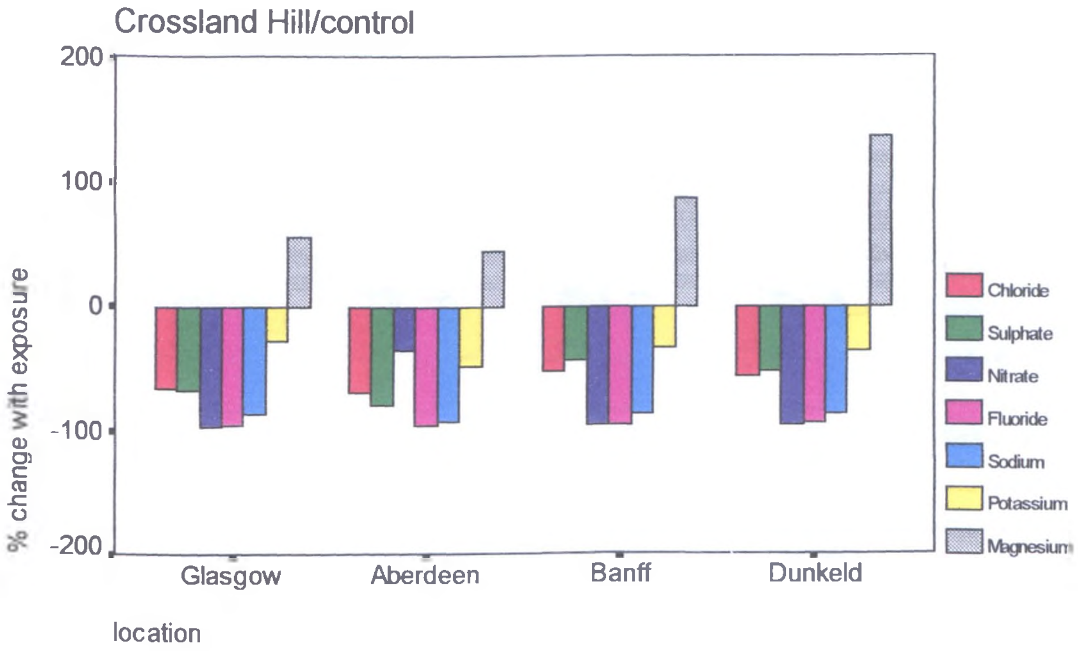


Figure 8.7a-b The percentage concentration change of the soluble ions before and after field exposure was calculated at each location (A) and the average at the four locations at depths 0-2, 2-5, 5-10 and 10-20 mm (B). Mean concentration before cleaning was subtracted from the mean concentration after cleaning and divided by the initial value: $(C_1 - C_0)/C_1*100$. Raw data in appendix 8.1.

(A)



(B)

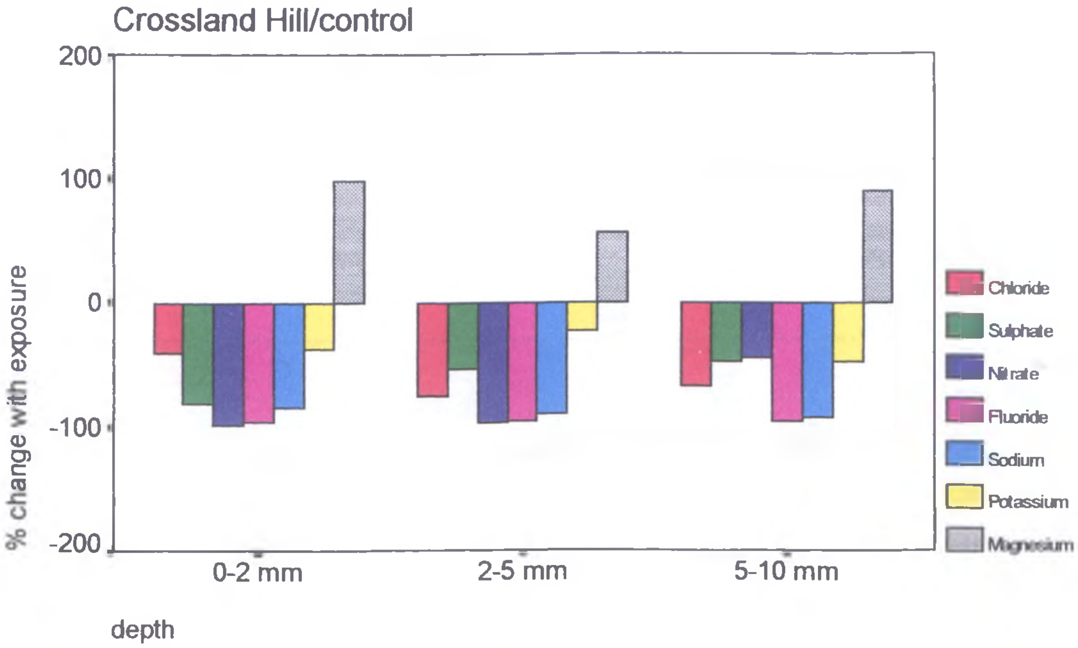
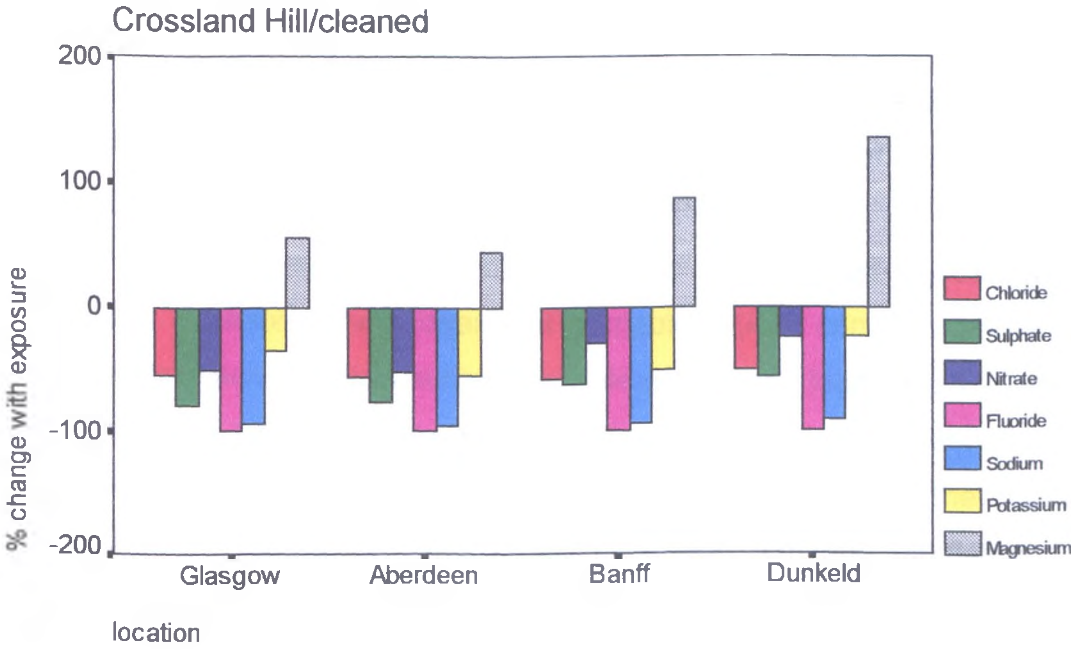


Figure 8.8a-b The percentage concentration change of the soluble ions before and after field exposure was calculated at each location (A) and the average at the four locations at depths 0-2, 2-5 and 5-10 mm (B). Mean concentration before cleaning was subtracted from the mean concentration after cleaning and divided by the initial value: $(C_1 - C_0)/C_1*100$. Raw data in appendix 8.1.

(A)



(B)

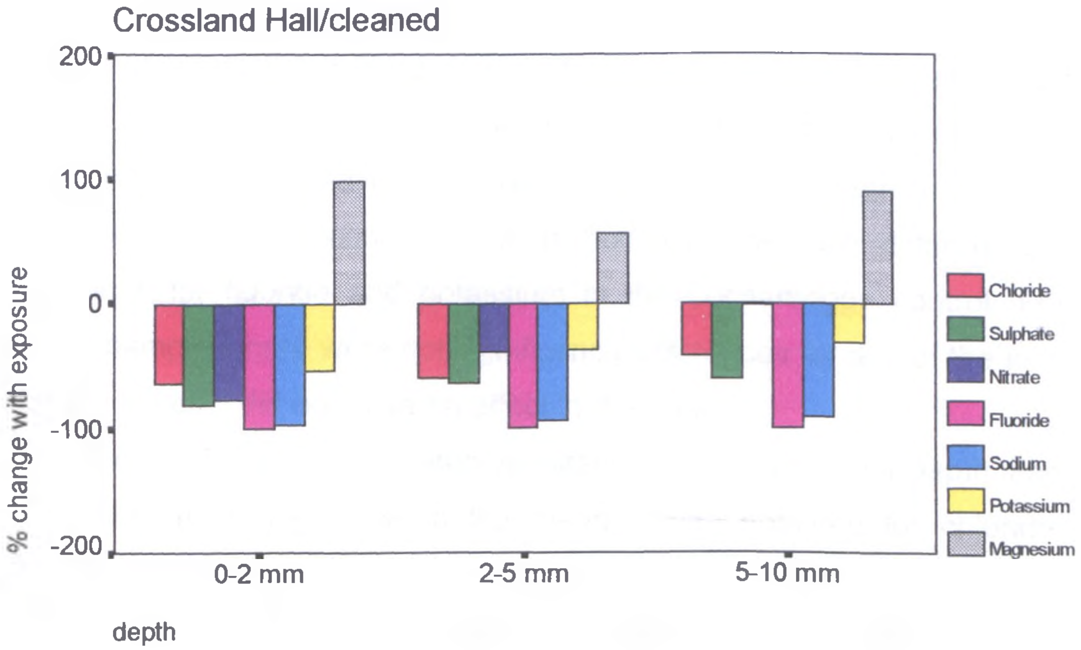


Figure 8.9a-b The percentage concentration change of the soluble ions before and after field exposure was calculated at each location (A) and the average at the four locations at depths 0-2, 2-5 and 5-10 mm (B). Mean concentration before cleaning was subtracted from the mean concentration after cleaning and divided by the initial value: $(C_1 - C_0)/C_1*100$. Raw data in appendix 8.1.

8.2.2 Statistical analysis

Statistical analysis of the data set from the depth profile (Appendix 8.1) involved comparison of mean values for the concentration of soluble ions and the method selected was one-way ANOVA (Section 3.8). In order to test whether the percentage change of the soluble ions differed significantly with depth and location, the dependent variables (ion concentrations) were compared for each between-subject variable (depth and location). The analysis of variance was calculated for each ion and the results for both sandstones are presented in Table 8.3a for the Locharbriggs and Table 8.3b for the Crossland Hill sandstone. One tailed F-test is used (Section 3.8), the tabulated critical values (Appendix 8.4) at the P = 0.05 level involves a 5% risk that the null hypothesis will be rejected even though it is true (Section 3.8). The F ratio is the between-groups mean square divided by the within-groups mean square. These values are compared to the output from the one-way analysis of variance. The results indicated a significant difference between the sample means for some of the ions. Altering the control factor "depth" lead to a significant difference between the mean values obtained for chloride and sulphate in the Locharbriggs control and for chloride, potassium and sodium in the cleaned sandstone. When the control factor is "location" then the differences were significance for fluoride and potassium in the Locharbriggs control. For the cleaned samples there were not significance differences for any of the ions and therefore location did not have an effect in this case.

For the Crossland Hill samples, altering the control factor depth lead to a significance difference between the mean values obtained for chloride and sodium in the control and for chloride, nitrate and sodium in the cleaned sandstone. When the control factor is location then the differences were significance for fluoride in Crossland Hill control. Again, for the cleaned samples there were no significance differences for any of the ions and therefore location did not have an effect on ion distribution.

The statistical analysis coincide with the observations reported previously for fluoride, potassium and chloride in the Locharbriggs control and nitrate in the Crossland Hill cleaned samples.

The analysis of variance showed no significant differences with location for any ion in both, Locharbriggs and Crossland Hill cleaned sandstones. These results do not agree with the graphical observations in the previous section that indicated there were significant differences for chloride and nitrate and the Locharbriggs sandstone and for magnesium, nitrate, potassium and sulphate in the Crossland Hill sandstone. Therefore, the groups compared graphically cannot be considered a proper way to predict significant differences between the mean values and must always be supported by an statistical analysis of the data.

Table 8.3a Comparison of means for the Locharbriggs sandstone using one-way ANOVA test.

ION	LOCHARBRIGGS CONTROL		LOCHARBRIGGS CLEANED	
	$F_{3,12}$ (DEPTH)	$F_{3,12}$ (LOCATION)	$F_{3,12}$ (DEPTH)	$F_{3,12}$ (LOCATION)
Chloride	20.04	0.045	22.48	0.19
Sulphate	6.6	0.78	0.24	0.06
Nitrate	2.13	2.47	0.98	3.32
Fluoride	0.55	5.28	2.57	2.25
Sodium	2.92	1.76	19.14	0.08
Potassium	0.26	25.83	5.36	0.98
Magnesium	na	na	na	na

na; data was not available

Table 8.3b Comparison of means for the Crossland Hill sandstone using one-way ANOVA test.

ION	CROSSLAND HILL CONTROL		CROSSLAND HILL CLEANED	
	$F_{2,9}$ (DEPTH)	$F_{3,8}$ (LOCATION)	$F_{2,9}$ (DEPTH)	$F_{3,8}$ (LOCATION)
Chloride	8.83	0.42	12.23	0.16
Sulphate	3.53	1.8	3.56	3.02
Nitrate	1.3	0.9	24.97	0.42
Fluoride	0.16	8.43	2.87	1
Sodium	11.57	0.75	9.76	0.85
Potassium	3.98	1.04	1.88	3.57
Magnesium	0.56	2.04	0.56	2.04

The correlation coefficients for the Locharbriggs control and cleaned sandstones (n=16), indicated a strong correlation between chloride and sulphate (0.7899) for the control samples and between sodium with chloride (0.7726) and potassium (0.7738) for the cleaned samples. Other results can be observed in Tables 8.4a-b. These correlations imply the existence of an atmospheric factor (acid rain for sulphates and seawater for chloride) and the natural weathering of softer minerals and clays containing potassium which will be mobilised and leached out the stone.

Table 8.4a Correlation coefficients for the Locharbriggs control sandstone.

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	0.1096	0.0138	-0.1284	-0.0424	0.7899**
Fluoride	0.1096	1.0000	0.6079*	0.4299	0.0799	0.4165
Nitrate	0.0138	0.6079*	1.0000	0.5038*	0.3528	0.2439
Potassium	-0.1284	0.4299	0.5038*	1.0000	0.4735	0.1226
Sodium	-0.0424	0.0799	0.3528	0.4735	1.0000	-0.1173
Sulphate	0.7899**	0.4165	0.2439	0.1226	-0.1173	1.0000

**P<0.001; *P<0.05; other values P>>0.05.

Table 8.4b Correlation coefficients for the Locharbriggs cleaned sandstone

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	0.1941	0.2363	0.5842*	0.7726**	0.0605
Fluoride	0.1941	1.0000	0.0703	0.5550*	0.3848	-0.2839
Nitrate	0.2363	0.0703	1.0000	0.3975	0.1552	0.3508
Potassium	0.5842*	0.5550*	0.3975	1.0000	0.7738**	0.0884
Sodium	0.7726**	0.3848	0.1552	0.7738**	1.0000	0.1661
Sulphate	0.0605	-0.2839	0.3508	0.0884	0.1661	1.0000

**P<0.001; *P<0.05; other values P>>0.05.

The Crossland Hill sandstone (n=12) presented different correlation coefficients for the control and cleaned samples. In the first case, sodium showed a strong correlation with chloride (0.7716). For the cleaned samples, sodium correlated well with the following anions: nitrate (0.9368), fluoride (0.8573) and sulphate (0.8342). Other results can be observed in Tables 8.5a-b. In this case, the correlations also indicate the effects of an atmospheric factor (acid rain for sulphates and nitrates and seawater for chloride) and the effects of chemical cleaning.

Table 8.5a Correlation coefficients for the Crossland Hill control sandstone.

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	0.3567	-0.2168	0.0461	0.7716*	-0.2587
Fluoride	0.3567	1.0000	0.1446	-0.2657	0.1528	0.0218
Magnesium	0.4253	0.4918	-0.5200	0.0307	0.3134	0.2250
Nitrate	-0.2168	0.1446	1.0000	-0.6234*	-0.5533	-0.2373
Potassium	0.0461	-0.2657	-0.6234*	1.0000	0.4243	0.2086
Sodium	0.7716*	0.1528	-0.5533	0.4243	1.0000	-0.2914
Sulphate	-0.2587	0.0218	-0.2373	0.2086	-0.2914	1.0000

**P<0.001; *P<0.05; other values P>>0.05.

Table 8.5b Correlation coefficients for the Crossland Hill cleaned sandstone

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	0.4118	0.7415*	0.5504	0.6787	0.5532
Fluoride	0.4118	1.0000	0.7614*	0.4778	0.8573**	0.6077*
Magnesium	0.0860	0.4070	0.1428	0.3993	0.3749	0.2304
Nitrate	0.7415*	0.7614*	1.0000	0.5632	0.9368**	0.8342**
Potassium	0.5504	0.4778	0.5632	1.0000	0.7163*	0.5756*
Sodium	0.6787*	0.8573**	0.9368**	0.7163*	1.0000	0.7841*
Sulphate	0.5532	0.6077*	0.8342**	0.5756*	0.7841*	1.0000

**P<0.001; *P<0.05; other values P>>0.05.

The preliminary treatment of the results through the method of correlation analysis showed that the values for the soluble ions could be used as an adequate number of independent variables for further statistical analysis by multivariate methods. These values together with the climatic variables (rainfall, temperature and gale wind) are use in the data matrix (Appendix 8.3). Application of the principal component analysis to the initial data matrix allowed the classification of the observations (percentage change) for each variable into two or more groups called principal components which are linear combinations of the initial variables. The principal component analysis reduces the number of variables included in the data matrix by establishing linear combinations between those variables that explain most of the variance.

The data matrix contained 16 sampling points for Locharbriggs and 12 sampling points for Crossland Hill and ten independent variables. In all cases, the sum of variance represented by the first two principal components was more than 60% of the total (Appendix 8.6) and therefore the initial variables were plotted in a two-dimensional diagram (Moropoulou *et al.,* 1995). Finally, the classification of variables as a function of location was attempted by using discriminant analysis. This analysis used as data vector the same variables and entered a numerical value for the classification factor: 1-Glasgow; 2-Aberdeen; 3-Banff and 4-Dunkeld.

The biplot for the first two principal components showed the distribution of the original variables (Figures 8.10-8.13a-c). The original variables intersect at (0, 0). The length of each vector is proportional to its contribution to the principal components and the angle between any two of them is inversely proportional to the correlation between them. The plot of discriminant functions values showed the distribution of the observations by location (Figures 8.10-8.13d).

The biplot of the three principal components extracted for the Locharbriggs control samples showed the distribution of the original variables (Figure 8.10a-c). In Figure 8.10a, a combination of climatic variables (Factor 1) and sulphate and chloride (Factor 3). A second factor is dominated by potassium, sodium and nitrate (Figures 8.10b-c). These three factors explain more than 80% of the variance (Appendix 8.6) and can be interpreted as climatic factor (factor 1), salt residues (factor 2) and sea water/external (factor 3). The scatter-plot of discriminant functions allowed a clear classification between urban and rural locations of the four locations (Figure 8.10d).

The biplot of the principal components for the Locharbriggs cleaned samples showed the distribution of the original variables (Figure 8.11a-c). Also here, an 80% of the variance in the results can be explained by three factors: a climatic factor, the combination of sodium, chloride and potassium (proximity to the sea) and the combination of sulphate and nitrate (proximity to urban sites). The plot of discriminant functions (Figure 8.11d) showed group 1 and 2 (urban sites) clearly separated from group 3 and 4 (rural sites).

The biplot of the principal components for the Crossland Hill control samples (Figure 8.12a-c) showed the original variables very scattered across the diagram. Three main factors can explain 84% of the variations on the distribution of ions in this stone (Appendix 8.6). These factors are interpreted as a climatic factor (factor 1) which is weakly correlated to any other variable. Second factor, dominated by potassium (mineral weathering) and third factor, a combination of sodium and chloride (proximity to the sea). Discriminant analysis (Figure 8.12d) showed discrimination between urban and rural sites and between coastal and inland sites.

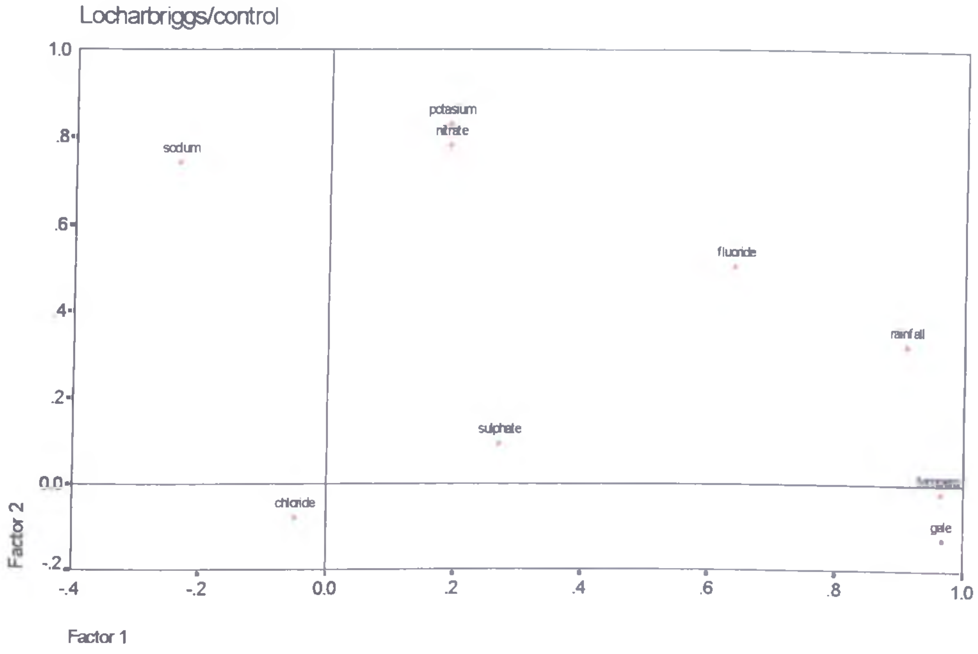
The biplot of the principal components for the Crossland Hill cleaned samples (Figure 8.13a-c) showed that distribution of ions is mainly dominated by a group of soluble ions, sodium, chloride, nitrate and sulphate, which are strongly correlated (Factor 1). This group of ions can represent the previous salt load in the stone and/or the influence of sea water. There is a climatic factor (Factor 2) and a third factor includes magnesium and some influence from potassium and therefore can be interpreted as a mineral decay factor. These three factors explain 87% of the variance in the results. The plot of discriminant functions (Figure 8.13d) showed again, the four groups clearly separated. Here, there was discrimination between urban-rural sites and between coastal-inland sites.

The principal component analysis on the Locharbriggs sandstone indicated that three main factors can explain over 80% of the variance in the results. By looking at the rotated factor matrix (Appendix 8.6), these three factors were interpreted as: influence of climate (Factor 1), potassium and sodium associated to mineral decay (Factor 2) and sulphate from external source (Factor 3). The climatic variables are introduced in the data matrix and they varied with location as shown in Appendix 8.3. Potassium and sodium can be associated to the weathering of the sandstone as both are mineral components of clays and feldspars which have weathered during exposure and release these ions within the stone. The contribution of fluoride cannot be associated to post-cleaning residues because it appears in both the control and the cleaned samples so it can only be another product of the weathering of minerals which contain fluoride (biotite mica). Finally, sulphate is present in the stone prior exposure and its contribution together with chloride in the control samples and nitrate in the cleaned samples can be interpreted as the initial salt load.

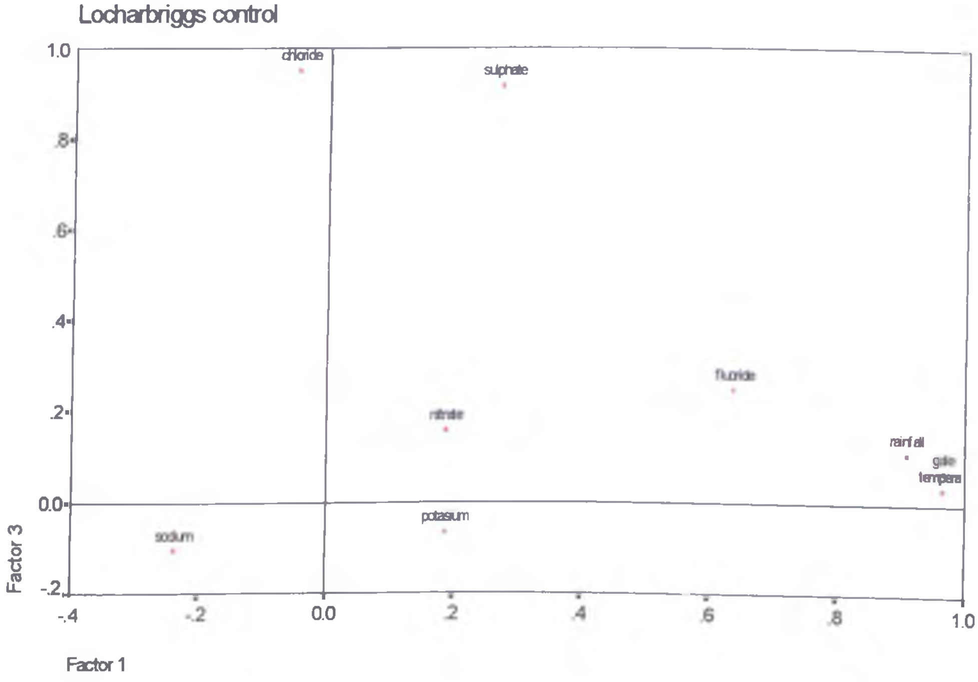
The principal component analysis on the Crossland Hill sandstone also extracted three main factors that explain over 80% of the variance in the results. By looking at the rotated factor matrix (Appendix 8.6), these three factors were slightly different for the control and the cleaned samples. Control samples were explained by a climatic factor, potassium as a mineral decay factor and sodium-chloride as a possible external salt load factor. The cleaned samples showed a first factor which was the combination of multiple ions and probably represented the salt load in the samples, the second factor was a climatic one and finally, the third factor with magnesium and potassium was considered to be related to the weathering of mineral components.

Discriminant analysis as a function of location indicated that Locharbriggs control and chemically cleaned sandstones are mainly controlled by a rural-urban factor. The same analysis for Crossland Hill sandstone indicated that both, rural-urban and coastal-inland factors are equally important for the control and cleaned samples.

(A)


Locharbriggs/control
1.0
.8
.6
.4
.2
0.0
-.2
Factor 2
-.4
-.2
0.0
.2
.4
.6
.8
1.0
Factor 1
potasium
nitrate
sodium
fluoride
rainfall
sulphate
chloride
tempera
gale

(B)


Locharbriggs control
1.0
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.6
.4
.2
0.0
-.2
Factor 3
-.4
-.2
0.0
.2
.4
.6
.8
1.0
Factor 1
chloride
sulphate
fluoride
nitrate
rainfall
gale
tempera
potasium
sodium

(C)

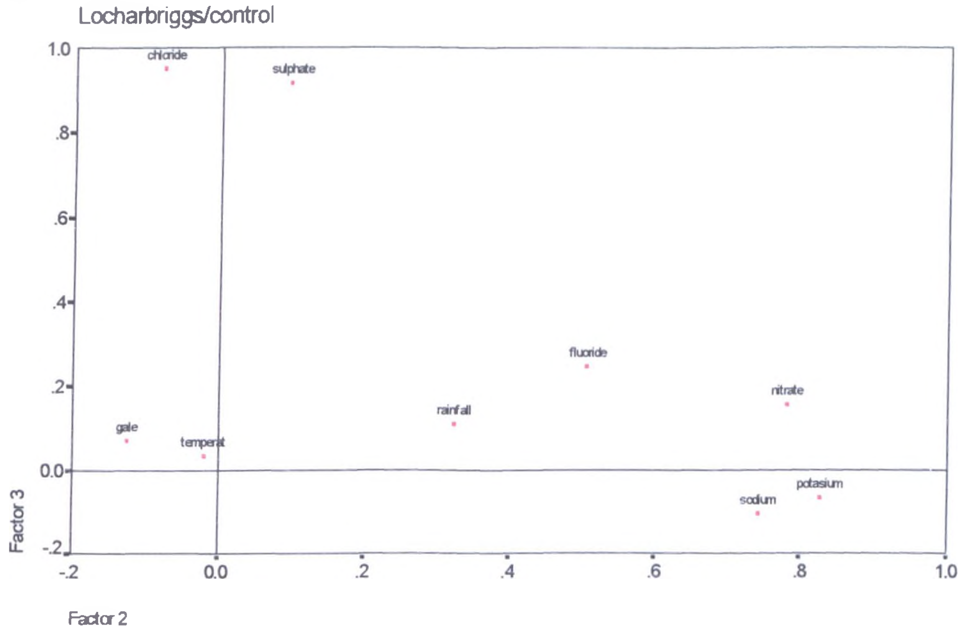


Figure 8.10a-c Biplot of the three principal components for the control Locharbriggs sandstone.

(D)

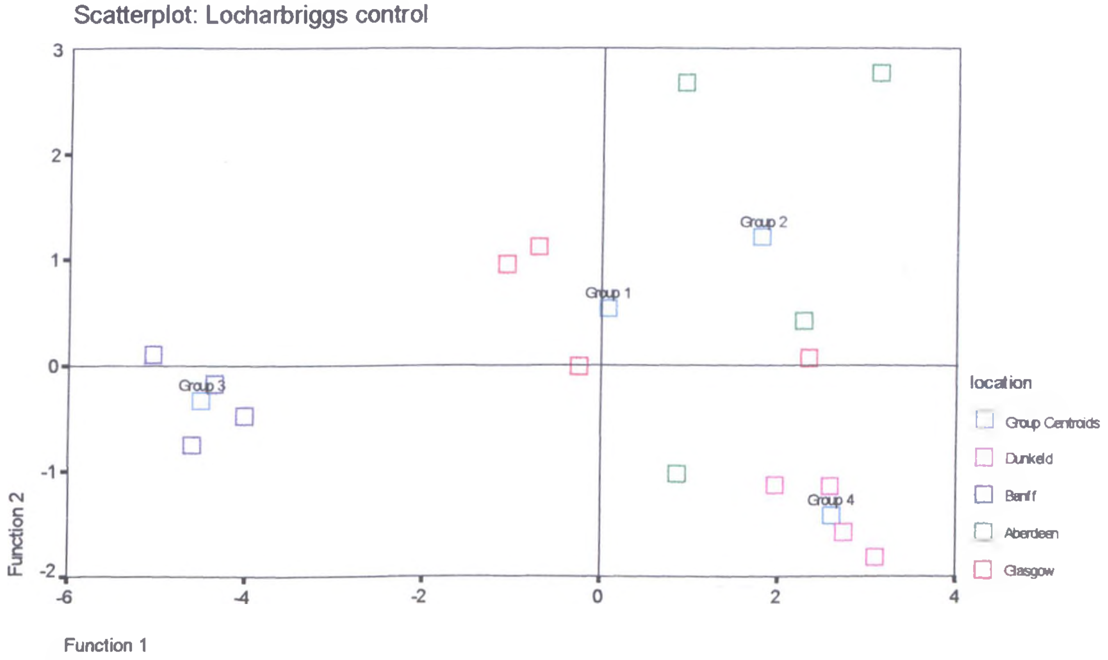
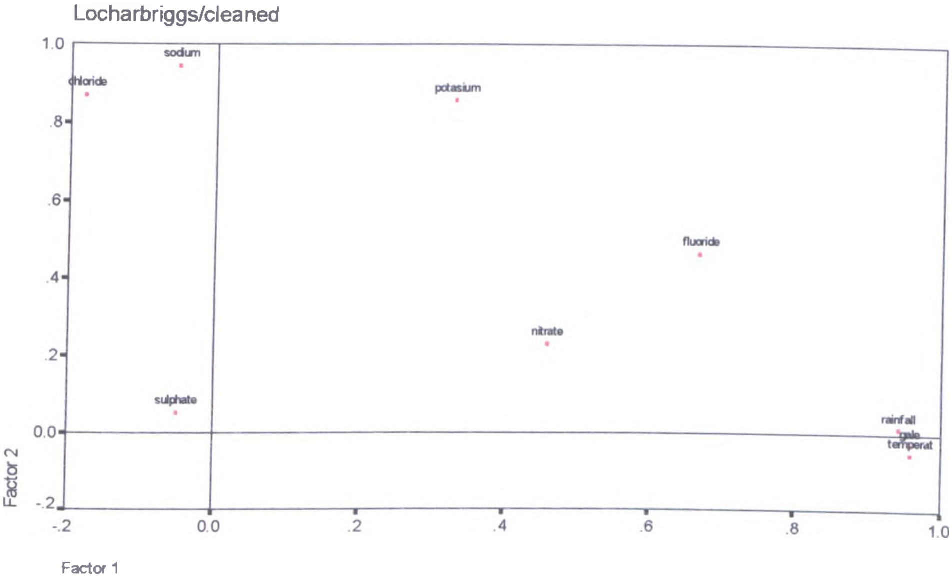
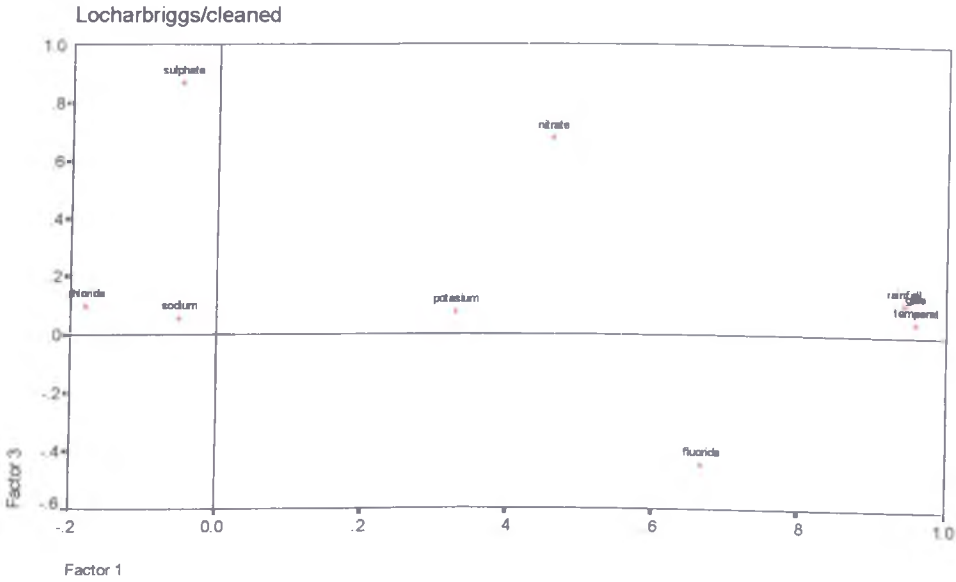


Figure 8.10d Scatter-plot of discriminant functions for the control Locharbriggs sandstone. Each group number represents a field site: 1 (Glasgow); 2 (Aberdeen); 3 (Banff) and 4 (Dunkeld)

(A)


Locharbriggs/cleaned
sodium
chloride
potasium
fluoride
nitrate
sulphate
rainfall
gale
temperat
1.0
.8
.6
.4
.2
0.0
-.2
Factor 2
-.2
0.0
.2
.4
.6
.8
1.0
Factor 1

(B)


Locharbriggs/cleaned
sulphate
nitrate
chloride
sodium
potasium
rainfall
gale
temperat
fluoride
1.0
.8
.6
.4
.2
0
-.2
-.4
-.6
Factor 3
-.2
0.0
.2
.4
.6
.8
1.0
Factor 1

(C)

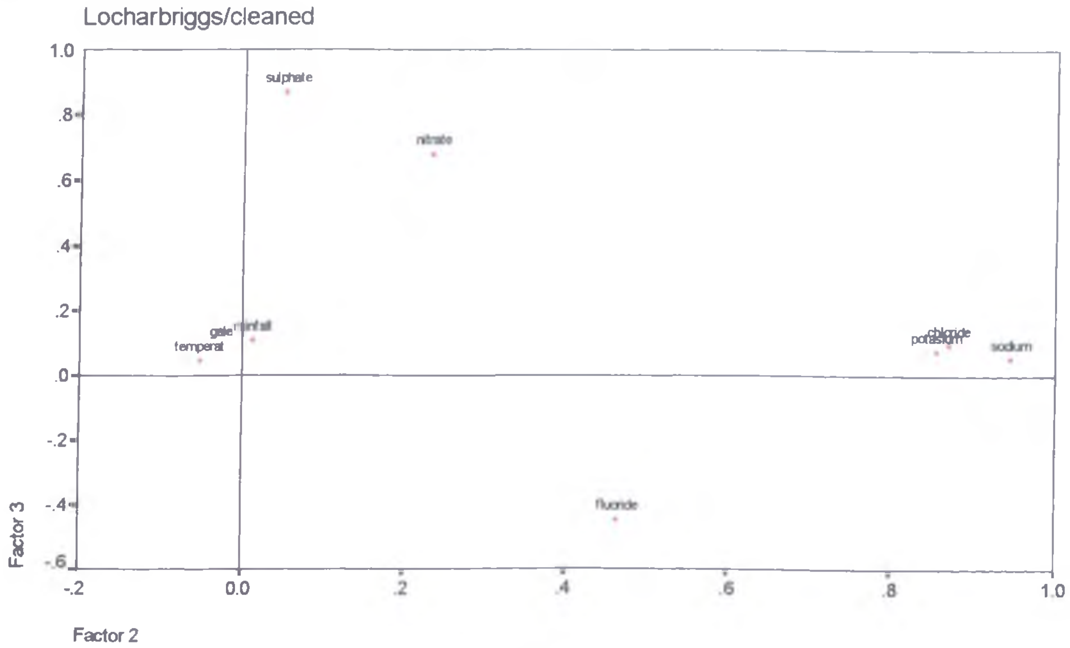


Figure 8.11a-c Biplot of the three principal components for the cleaned Locharbriggs sandstone.

(D)

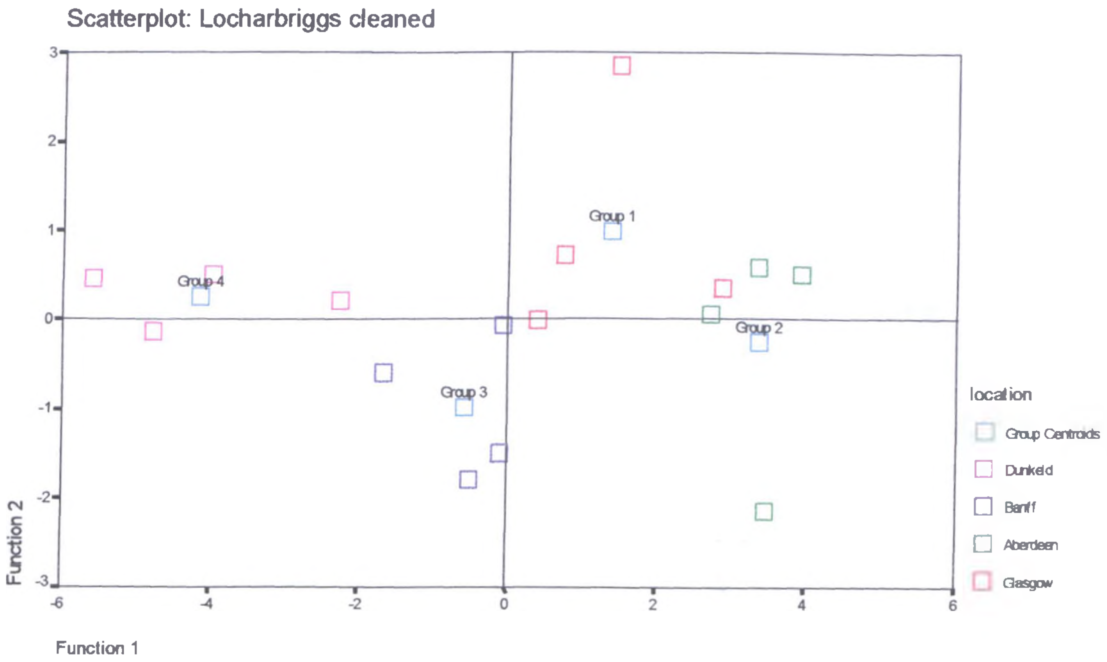
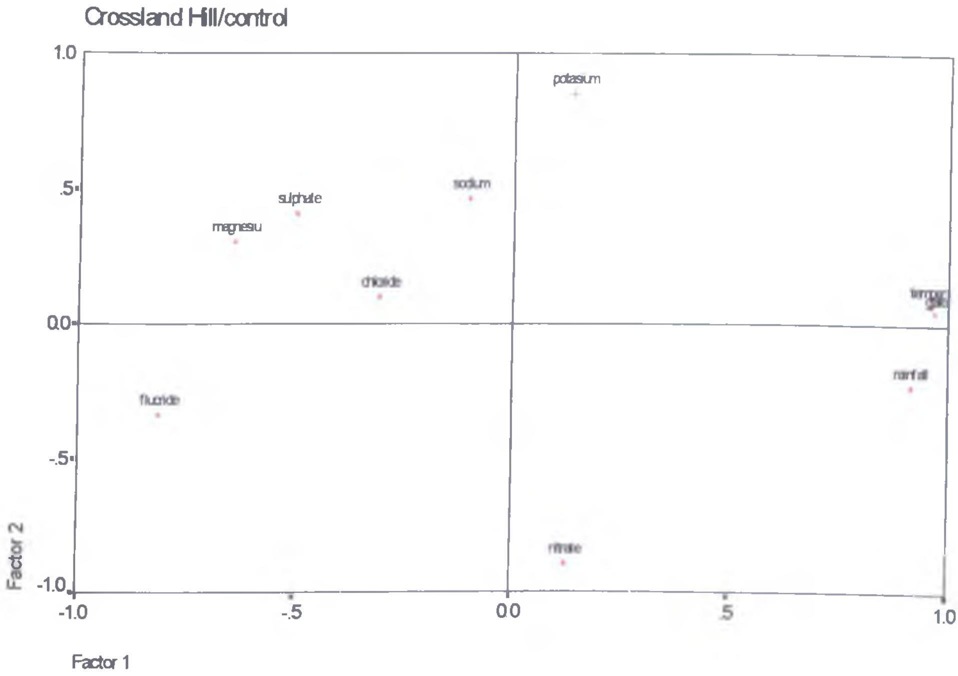
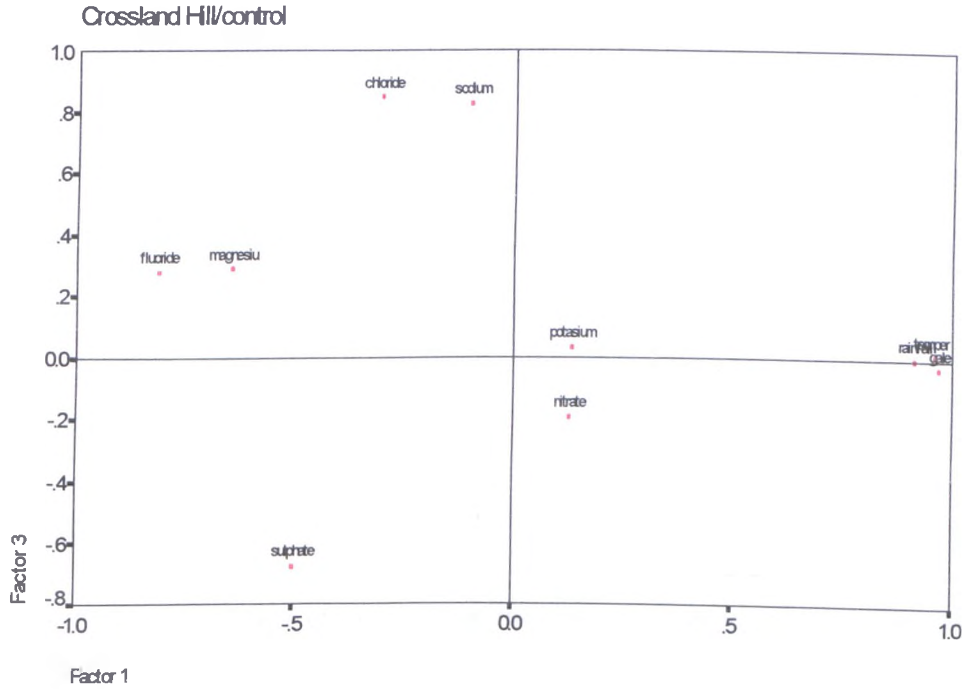


Figure 8.11d Scatter-plot of discriminant functions for the cleaned Locharbriggs sandstone. Each group number represents a field site: 1 (Glasgow); 2 (Aberdeen); 3 (Banff) and 4 (Dunkeld)

(A)


Crossland Hill/control
potasium
sodium
sulphate
magnesiu
chloride
temper
gale
rainfall
fluoride
nitrate
1.0
.5
0.0
-.5
-1.0
Factor 2
-1.0
-.5
0.0
.5
1.0
Factor 1

(B)


Crossland Hill/control
chloride
sodium
fluoride
magnesiu
potasium
rainfall
temper
gale
nitrate
sulphate
1.0
.8
.6
.4
.2
0.0
-.2
-.4
-.6
-.8
Factor 3
-1.0
-.5
0.0
.5
1.0
Factor 1

(C)

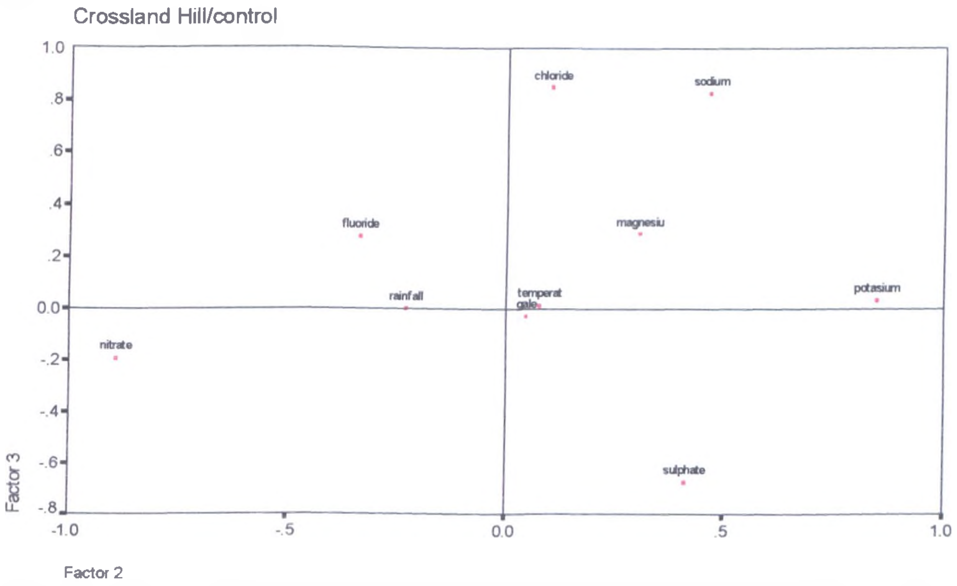


Figure 8.12a-c Biplot of the three principal components for the control Crossland Hill sandstone.

(D)

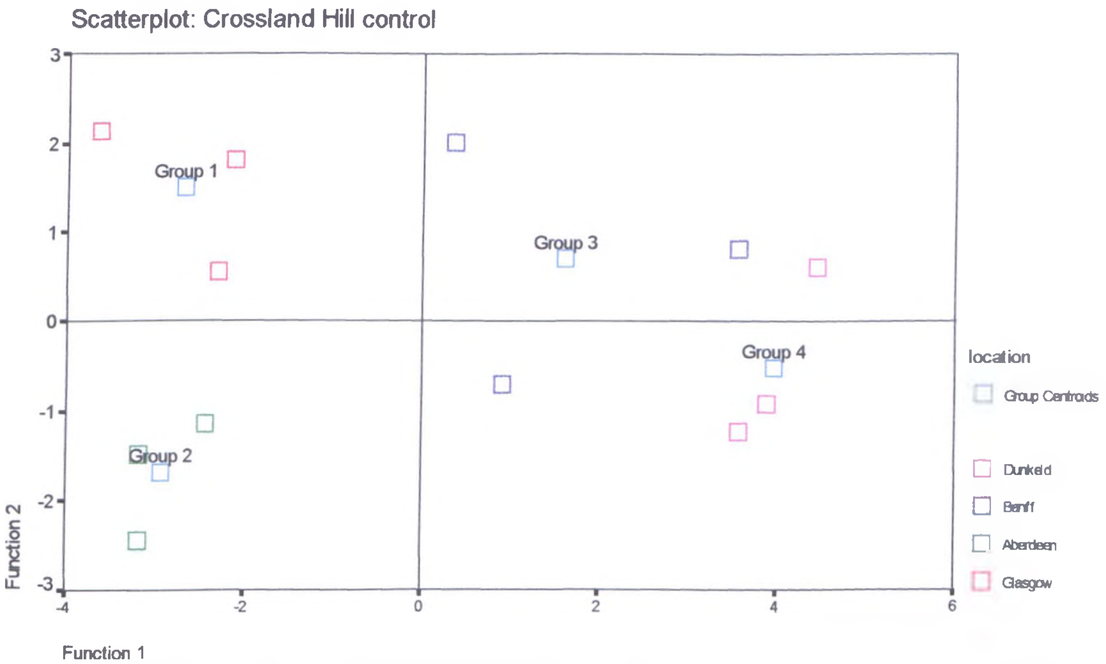
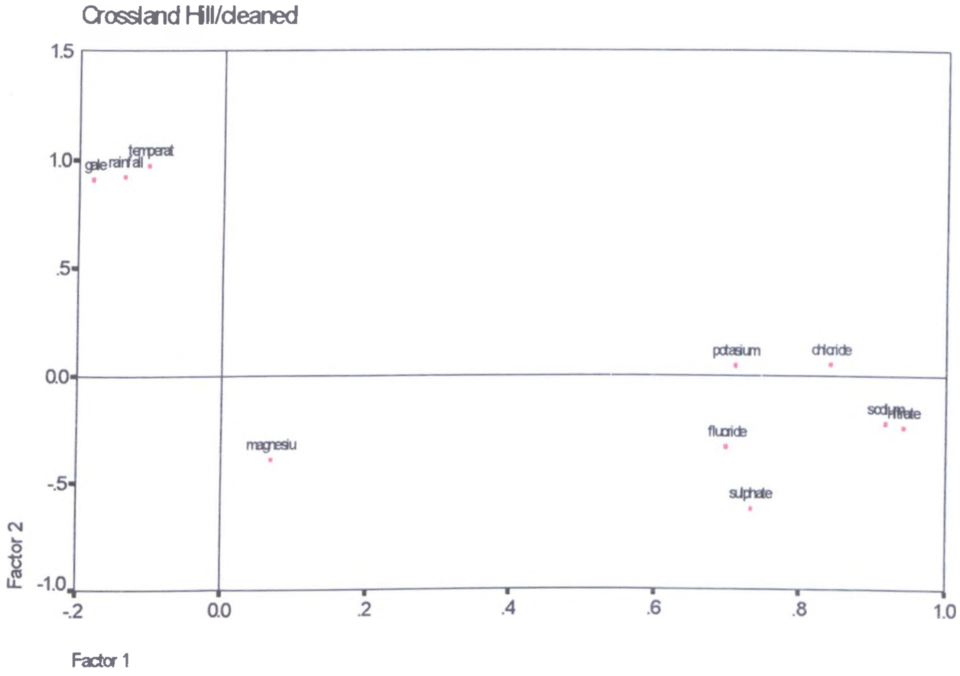
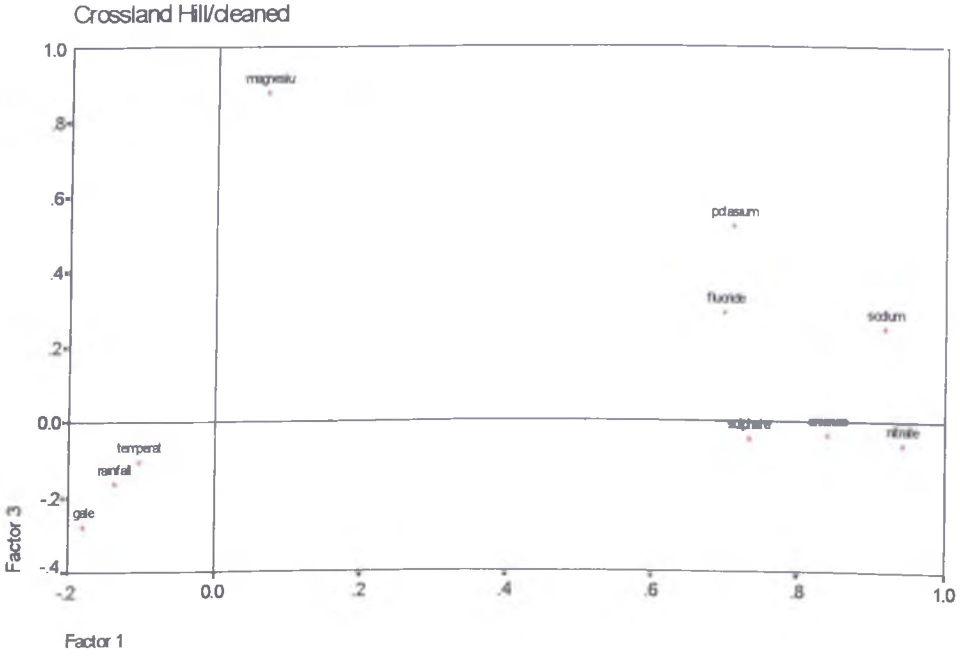


Figure 8.12d Scatter-plot of discriminant functions for the control Crossland Hill sandstone. Each group number represents a field site: 1 (Glasgow); 2 (Aberdeen); 3 (Banff) and 4 (Dunkeld).

(A)


Crossland Hill/cleaned
1.5
1.0
.5
0.0
-.5
-1.0
Factor 2
-.2
0.0
.2
.4
.6
.8
1.0
Factor 1
temperat
gale
rainfall
potasium
chloride
sodium
nitrate
fluoride
magnesiu
sulphate

(B)


Crossland Hill/cleaned
1.0
.8
.6
.4
.2
0.0
-.2
-.4
Factor 3
-.2
0.0
.2
.4
.6
.8
1.0
Factor 1
magnesiu
potasium
fluoride
sodium
sulphate
nitrate
temperat
rainfall
gale

(C)

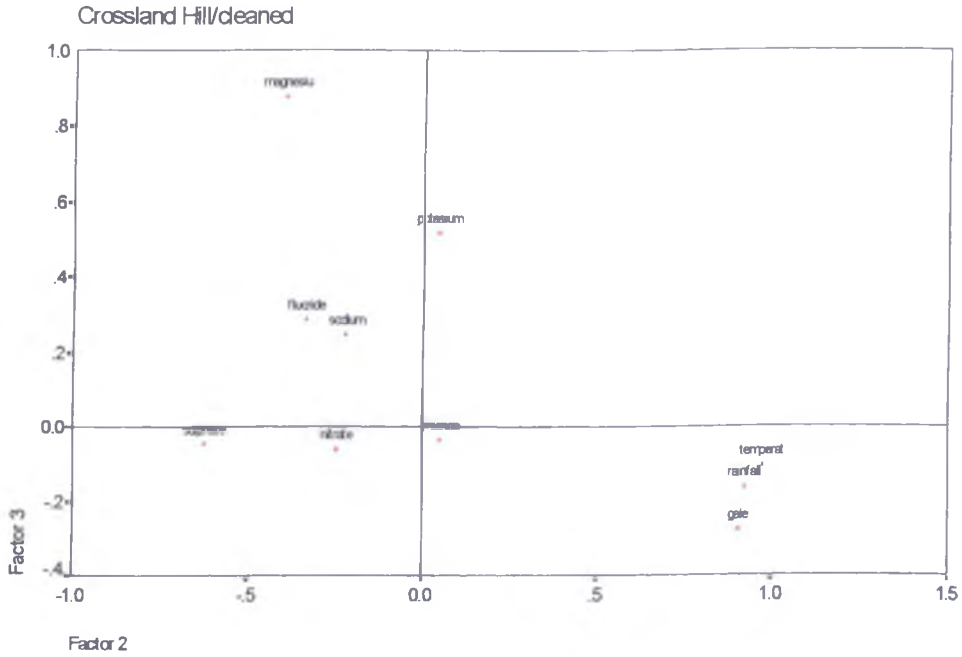


Figure 8.13a-c Biplot of the three principal components for the cleaned Crossland Hill sandstone.

(D)

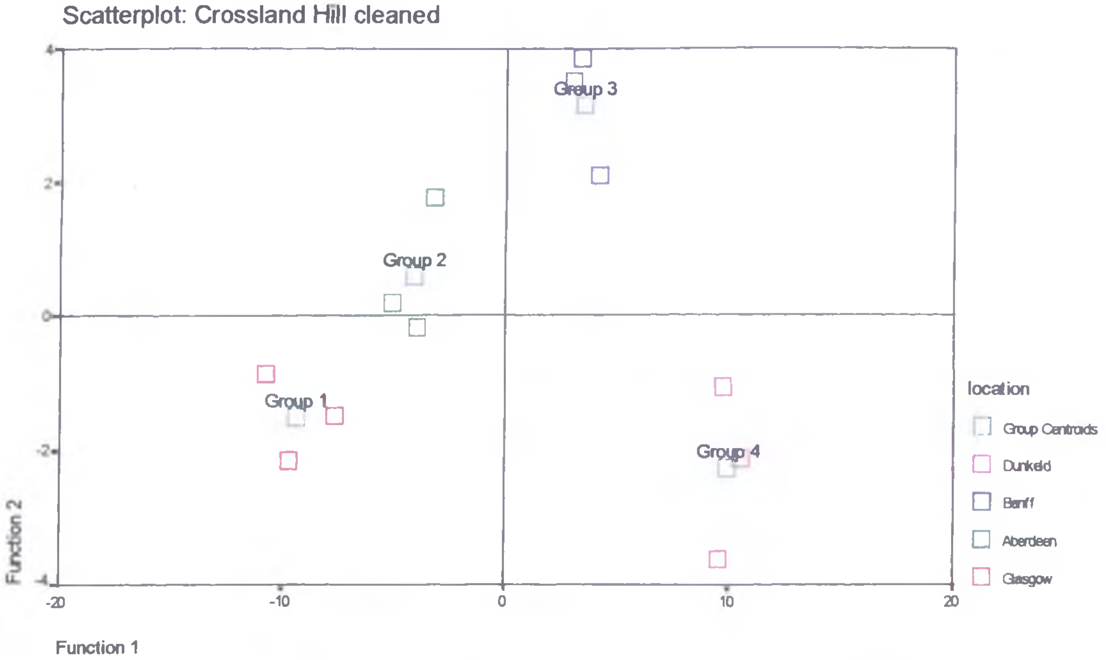


Figure 8.13d Scatter-plot of discriminant functions for the cleaned Crossland Hill sandstone. Each group number represents a field site: 1 (Glasgow); 2 (Aberdeen); 3 (Banff) and 4 (Dunkeld).

8.2.3 Summary

Before exposure both, Locharbriggs and Crossland Hill sandstones, were chemically cleaned and post-cleaning residues were found, especially fluoride and sodium (see Chapter 5). Additionally, previous exposure history of the stones might have left a number of salts in the stone matrix (e.g. chloride, nitrate and sulphate). During the study, the stone samples were exposed to continuous wetting/drying cycles and other natural weathering processes which affected the dissolution of minerals and therefore the mobilisation or distribution of certain ions such as potassium and magnesium. Additionally, there are external factors such as proximity to the sea or atmospheric pollution which probably contributed to the incorporation of external elements (e.g. chloride, sulphate and nitrate).

Although it is very difficult to reach general conclusions from a small data set, it was observed a different distribution in depth and with location for selected soluble ions. These differences were compared statistically by using analysis of variance. The statistical analysis confirmed some of the observations but it also suggested that independently of having a control not cleaned or a chemically cleaned sample, most ions presented a similar distribution for all field sites.

The principal component analysis allowed the classification of the dependent variables (soluble ions and climatic values) into two or three factors which explained between 60-80% of the total variance. Two-dimensional diagrams of the factors showed the distribution for the original variables and helped to predict what type of soluble ions will play a more important role in the weathering of a sandstone as a function of location. One common factor was shared in all the analysis. This was the combination of the three climatic variables (rainfall, temperature and gale wind). The second factor varied depending on the type of sandstone and probably relates to the weathering of the mineral components (potassium, sodium, magnesium and fluoride). Finally, a third factor was extracted which accounted for a number of ions probably related to the previous natural exposure of the stones and interpreted as a salt load (e.g. sulphate, nitrate and chloride).

The observations in the data matrix were also analysed by discriminant analysis. This showed how urban-rural and inland-coastal field sites can be considered very important controlling factors. The differences found related to the type of sandstone and not the cleaning regime imposed on the stone. This means that in the case of the Locharbriggs sandstone, the urban-rural factor is the only one controlling the distribution of observations as in the Crossland Hill, both, urban-rural and inland-coastal factors, equally control the distribution. Additionally, discriminant analysis allow for new observations to be added in the original data matrix and be further classified as a function of location.

8.3 Analysis of soluble residues after leaching

The modified method was adopted from a desalination study commonly used in conservation (Section 3.4). Field-exposed samples were immersed for one month in 3000 mL of deionised water in closed plastic containers, and salt removal was monitor for one month by sampling aliquots of 30 mL. Mechanical stirring was applied during all the time. The results were compared to the leaching trends prior to field exposure (Section 5.2). Only one chemically cleaned sample from each location was used for the experiment. Two analysis were undertaken for each ion at times 0, 5, 15 and 30 days. The results were normalised by dividing them by a factor m/V, where m is the weight in grams of the stone sample and V the volume of immersion water in litres. Since in all cases, for the same stone type, samples from the original block were used in the studies, the trends observed indicate the influence of location on the leaching trends and are not due to variation in the sandstone itself.

The ions selected for chemical analysis (sodium, potassium, magnesium, sulphate, nitrate, chloride and fluoride) represent the main indicators of decay processes, associated with soluble salts. Results from replica leaching experiments before and after exposure were compared for the chemically cleaned samples. This was done by calculating the percentage change as the difference between the average values for the soluble ions leached before and after exposure over a period of 30 days. The sampling intervals were 0, 5, 15 and 30 days. Figures 8.14a-b and Figures 8.15a-b present these results for both sandstone types, Locharbriggs and Crossland Hill respectively.

The analysis of the Locharbriggs cleaned samples showed no significant variation with location for nitrate, fluoride and sodium (Figure 8.14a). In all sites, these ions decreased their concentration in water after exposure. Chloride and potassium increased their concentration significantly after exposure, especially at the urban sites (Glasgow and Aberdeen). This can be explained in terms of differences in the number of days with gale winds and snow between the urban and the rural sites (Section 3.7). This climatic factor would contribute to the external deposition of chloride on the surface of both sandstones. Sulphate and magnesium concentrations decreased after exposure in all field sites but Aberdeen where they increased.

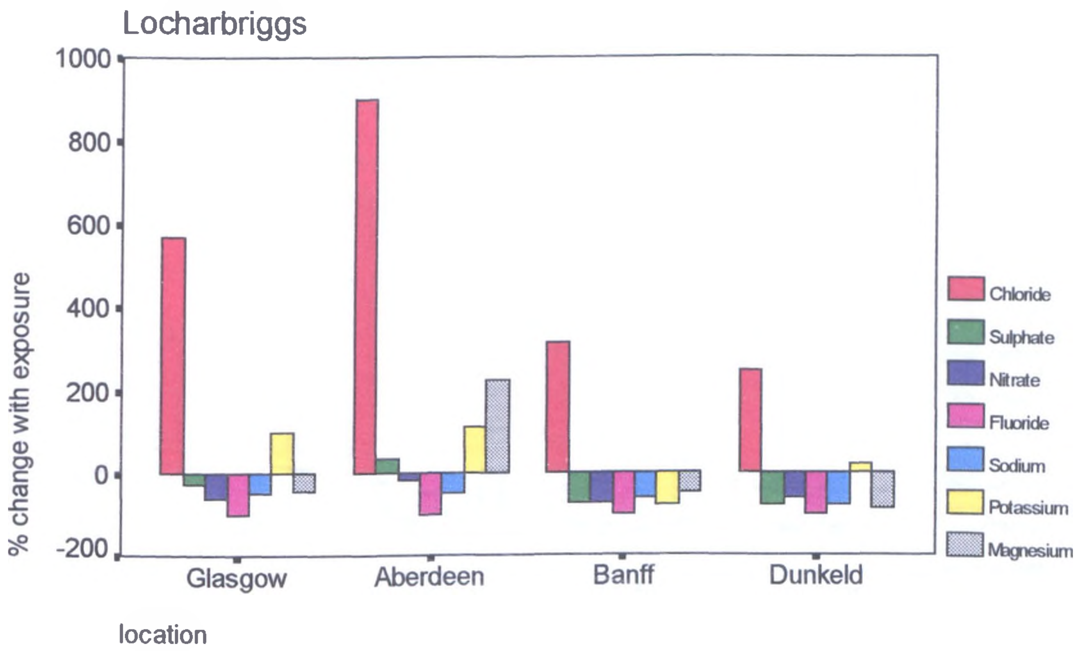
The results for the leaching as a function of time only showed significant differences for chloride and potassium (Figure 8.14b). The origin of this chloride is probably external (seawater aerosol) and it deposited in all field sites. Potassium most probably originates in the mineral components. After 5 days leaching, all ions seemed to reach an equilibrium.

The analysis of percentage change with location for the Crossland Hill sandstones (Figure 8.15a) showed significant changes for most of the ions. Chloride, magnesium and fluoride increased their concentrations in water after exposure and the percentage change was dependent on location. Sulphate only increased in Aberdeen and did not change significantly in the other field sites. Nitrate, sodium and potassium decreased their concentrations after exposure at all field sites.

The percentage change of leached ions with time was significant for chloride, magnesium and fluoride (Figure 8.15b) which increased their concentration in water after exposure. As in Locharbriggs sandstone, the origin of this chloride can be found in seawater aerosol. The magnesium and fluoride are most likely originated in the stone mineral components as a result of the dissolution of feldspars and micas.

The 24 month-exposure may have increased the weathering of the mineral components in the stone and also deposited external ions, such as chloride, sulphate and nitrate. In general, gains or losses in concentration in the leachate when compared to the initial trend prior exposure can be related to the tendency of the ions to leach more easily from the most vulnerable and decayed mineral components. In the Locharbriggs, potassium originates in the clays and feldspars mainly and after exposure the tendency to leach out the stone was larger. The same is observed for the Crossland Hill with magnesium and fluoride, which mainly originate in the mica component and leach more readily after exposure. In both cases, concentrations of these soluble components in water were larger after field exposure so it can be concluded that weathering was induced after exposure. If the ions were originated from an external source, as it is suggested for chloride then, the leaching after field exposure would be similar for both sandstones. This trend was confirmed so that it can be concluded that a percentage of chloride in the sandstones was acquired externally and leached out from the stone after exposure. The differences between field sites were associated to a climatic factor.

(A)



(B)

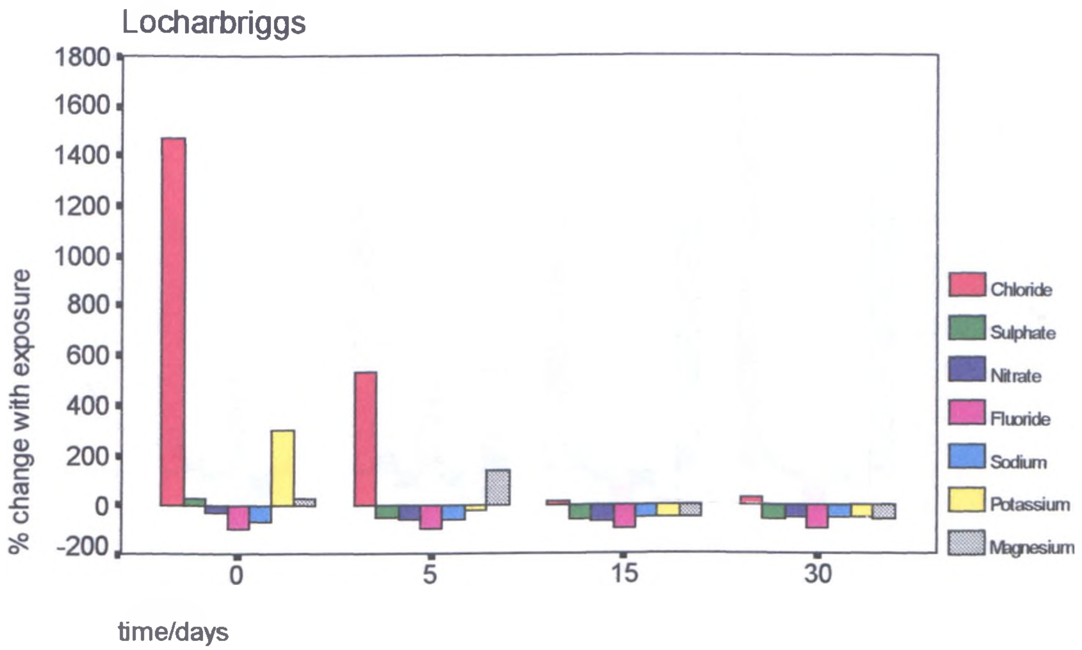


Figure 8.14a-b Mean percentage change in the leaching of soluble ions over a period of 30 days. The values were calculated as the difference between the cumulative normalised values for the cleaned samples before and after exposure. Raw data in appendix 8.2.

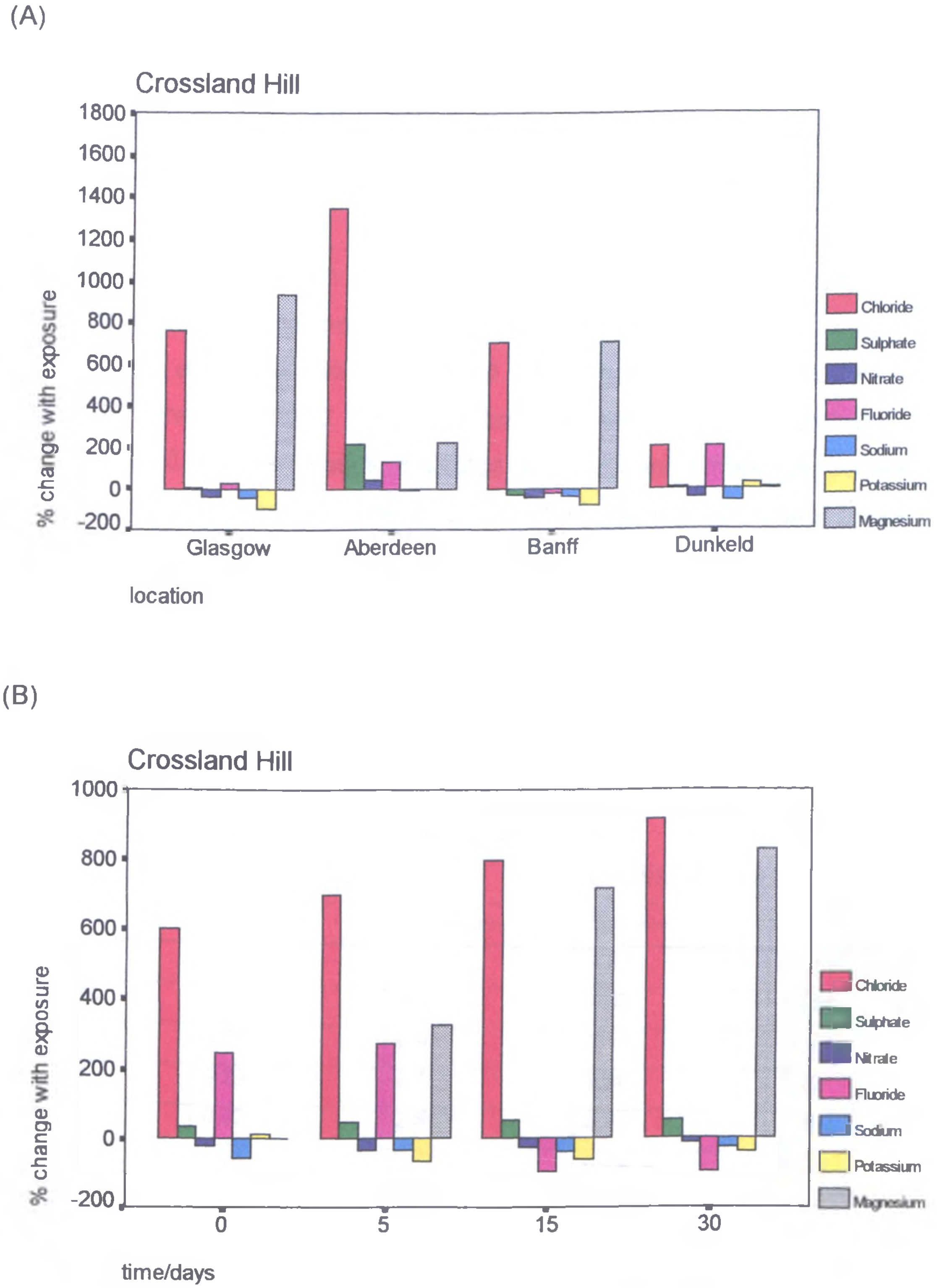


Figure 8.15a-b Mean percentage change in the leaching of soluble ions over a period of 30 days. The values were calculated as the difference between the cumulative normalised values for the cleaned samples before and after exposure. Raw data in appendix 8.2.

8.3.1 Statistical analysis

Statistical analysis of the results involved comparison of means and the method selected was one-way ANOVA. In order to test whether the percentage change with exposure differed significantly with time and location, the dependent variables (ion concentrations) were compared for each between-subject variable (time and location). Results for the different ions in both sandstones are presented in Table 8.6. The critical tabulated value $F_{3,12}$= 3.49 (P=0.05, one-way tailed test) can be compared to the calculated values (Appendix 8.4). The results indicated a significant difference between the sample means for some of the ions. Therefore altering the control factor "time" lead to a significance difference between the mean values obtained for chloride and potassium in the Locharbriggs sandstone and for fluoride in Crossland Hill sandstone. When the control factor is "location" then the differences were significant for nitrate, fluoride and magnesium in Locharbriggs and for all ions but fluoride and magnesium in Crossland Hill.

Table 8.6 Comparison of means using one-way ANOVA test.

ION	LOCHARBRIGGS		CROSSLAND HILL	
	$F_{3,12 \text{ (time)}}$	$F_{3,12 \text{ (location)}}$	$F_{3,12 \text{ (time)}}$	$F_{3,12 \text{ (location)}}$
Chloride	6.97	0.53	0.29	21.09
Sulphate	2.07	3.76	0.02	52.85
Nitrate	1.71	6.44	0.15	32.61
Fluoride	0.82	4.7	7.38	0.73
Sodium	0.52	2.54	0.71	4.75
Potassium	5.78	0.72	0.74	3.98
Magnesium	1.09	4.84	1.58	2.28

The correlation coefficients for the Locharbriggs sandstone (n=16), indicated a strong correlation between potassium with chloride (0.7627) and sulphate (0.7584). Nitrate correlated well with sulphate (0.8294). Other results can be observed in Table 8.7. These correlations imply the existence of an atmospheric factor (acid rain for sulphates and nitrates and seawater for chloride) and the natural weathering of softer minerals and clays containing potassium which will be mobilised and leached out the stone.

Table 8.7. Correlation coefficients for Locharbriggs cleaned sandstone

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	0.5654*	0.6721*	0.7627**	0.1254	0.8418**
Fluoride	0.5634*	1.0000	0.7006*	0.5553*	0.3193	0.5492*
Magnesium	0.4403	0.4832	0.5115*	0.3047	0.3005	0.5625*
Nitrate	0.6721*	0.7006*	1.0000	0.5856*	0.0703	0.8294**
Potassium	0.7627**	0.5553*	0.5856*	1.0000	0.0374	0.7584**
Sodium	0.1254	0.3193	0.0703	0.0374	1.0000	0.2153
Sulphate	0.8418**	0.5492*	0.8294**	0.7584**	0.2153	1.0000

$^{**}P<0.001$; $^{*}P<0.05$; other values P>>0.05.

The Crossland Hill sandstone (n=16) presented similar correlation coefficients. In this case sodium showed a strong correlation with chloride (0.8879), sulphate (0.7265) and nitrate (0.6910). Nitrate correlated with sulphate (0.9558). Other results can be observed in Table 8.8. In this case the correlations also indicate the effects of an atmospheric factor (acid rain for sulphates and nitrates and seawater for chloride) and the natural weathering of softer minerals containing sodium which will be mobilised and leached out the stone.

Table 8.8. Correlation coefficients for Crossland Hill chemically cleaned sandstone

ION	Chloride	Fluoride	Nitrate	Potassium	Sodium	Sulphate
Chloride	1.0000	-0.2100	0.8264**	-0.0221	0.8879**	0.7872**
Fluoride	-0.2100	1.0000	-0.009	0.5977*	-0.0612	0.1309
Magnesium	0.2470	-0.3952	-0.2086	-0.3953	0.2765	-0.2493
Nitrate	0.8264**	-0.0009	1.0000	0.3068	0.6910*	0.9558**
Potassium	-0.0221	0.5977*	0.3068	1.0000	0.1689	0.3747
Sodium	0.8879**	-0.0612	0.6910*	0.1689	1.0000	0.7265**
Sulphate	0.7872**	0.1309	0.9558**	0.3747	0.7265**	1.0000

$^{**}P<0.001$; $^{*}P<0.05$; other values P>>0.05.

The analysis of individual values for the concentration of soluble ions in leachate were presented separately for the anions and cations (Appendix 8.2-b). The cumulative trends at four different times can be observed separately for the urban sites (Glasgow and Aberdeen) and for the rural sites (Banff and Dunkeld).

After 30 days of leaching in water, the combined concentrations of anions from the Locharbriggs sandstone totalled 50 mg/L in Glasgow and almost 60 mg/L in Aberdeen. On the other hand, these values decreased to 10 and 17 mg/L for Banff and Dunkeld respectively. The values for the total amount of cations were 30 mg/L in Glasgow and Aberdeen. These values decreased to 28 mg/L and 8 mg/L in Banff and Dunkeld respectively (Appendix 8.2a).

The total amount of anions leached from the Crossland Hill sandstone was 50 mg/L in Glasgow, 120 mg/L in Aberdeen and 25 mg/L in Banff and Dunkeld. The values for the cations were 30 mg/L in Glasgow and Banff and values for the other two sites, Aberdeen and Dunkeld were not analysed (Appendix 8.2b).

What is observed for the Locharbriggs and Crossland Hill sandstones after exposure is that proximity to the sea only cannot explain why the two urban sites have the larger content of chloride. If this was the case then Banff should also present equal amounts of chloride. As explained above, this can be explained in terms of differences in the number of days with gale winds and snow between the urban and the rural sites (Section 3.7). This climatic factor would contribute to the external deposition of chloride on the surface of both sandstones. Other indicators such as sulphate and nitrate can be more clearly correlated to one particular site (Aberdeen) and therefore to the existence of atmospheric pollution. The mean air pollution levels for the period between 94-96 were of 127.2 $\mu g/m^3$ for NO_2 and 20 $\mu g/m^3$ for SO_2 (Section 3.7). Both within the EC limit set at 200 $\mu g/m^3$ and 100 $\mu g/m^3$ respectively but it can be suggested that high peak periods contributed to the deposition of these gases. Sodium and fluoride are leached out from all field sites with a similar trend for the Locharbriggs sandstone and therefore it can be interpreted as the leaching of to cleaning residues. For Crossland Hill, the correlation of these two indicators to cleaning residues is not that clear and probably the existence of biotite mica together with a low porosity explain the results.

There are reasons to suspect the difference in behaviour is related to differences in mineralogy and very probably content of clays. But also the porosity might play a very important role as indicated in Section 8.1.

The Crossland Hill sandstone has a higher proportion of feldspars and mica minerals which when weathered will release K, Na, Mg and F. Also here, these ions could reassamble or undergo displacement reactions with other anions such as sulphate, nitrate or chloride. In this case, the chloride indicator relates to proximity to the sea with Aberdeen giving the highest values followed by Banff and Glasgow very closely.

8.3.2 Summary

The average results from the leaching of soluble salts after field exposure showed an influence of the geographical location on the release of some of the ions selected. Therefore there are certain ions which are more affected by the location. For example, chloride is always higher in Aberdeen for both sandstones. Magnesium and potassium levels remained also higher for Locharbriggs sandstone after exposure in Aberdeen. In general, sulphate, nitrate, sodium and magnesium leached out more rapidly from Locharbriggs sandstone after exposure at rural sites (Banff and Dunkeld). The pattern changed for the Crossland Hill and here there was a larger variation between ions and also between locations, making it more difficult to reach general conclusions.

The differences for both sandstones can be related to their mineralogy and porosity as explained in previous sections but also the environment must play a role and therefore the location. The differences between the four sites are not only those related to urban-rural and/or coastal-inland site but also to climatic differences. The total yearly rainfall in Glasgow and Aberdeen is twice as in Banff and Glasgow. As explained by Keller *et al.*, (1963) the leaching rates for calcium, magnesium, sodium and potassium are higher in CO_2-charged waters or acidic waters. The resistance of the minerals to weathering will be influenced by the type and amount of water. Also the presence of marine aerosols might enhance this leaching as observed by Aires-Barrios *et al.*, (1975). A larger and more acidic rainfall (characteristic of urban sites) together with the presence of certain minerals such as clays, feldspars and muscovite mica could explain the differences in the leaching trends between sandstones and between locations.

The immersion in deionised water for 30 days is only an experimental approach to evaluate the trends of leachable ions. The statistical analysis by using one-way ANOVA recognised the existence of a significance difference in the mean values between times and some particular ions. In these cases, the control factors (location and time) explain the differences and the possibility of random error can be eliminated.

8.4 Investigation of colour changes after field exposure

Results from the colour changes before and after exposure were compared for both the control and chemically cleaned samples. This was done by calculating the percentage change as the difference between the average values (n=5) for the three colour components (L, a and b) before and after exposure for the Locharbriggs and Crossland Hill sandstones.

The colour changes of a freshly broken surface have been reported to vary from 53-61 (L), 1-2 (a) and 17-20 (b) (Urquhart *et al.,* 1995). Weathering, non-organic soiling and biological growth will affect the stone colour and therefore the value of the three colour components, brightness (L), red-green (a) and yellow-blue (b). Incremental changes larger than $\Delta L=8$, $\Delta a=2$ and $\Delta b=3$ can be related to changes in colour as a consequence of the exposure (Table 8.9). The results indicate the colour values have varied over time.

Table 8.9 Increment change in colour components with exposure. Values were calculated by substrating the initial value (t=0) from the final value (t=24) (eg., L_1-L_0).

CHANGES WITH FIELD EXPOSURE[1]							
Locharbriggs control	L	a	b	**Locharbriggs cleaned**	L	a	b
Glasgow (UI)	-20.38	4.25	3.3	Glasgow (UI)	-15.19	4.87	4.52
Aberdeen (UC)	-6.15	5.1	6.4	Aberdeen (UC)	-15.21	6.06	5.24
Banff (RC)	-16.39	7.6	6.79	Banff (RC)	-15.63	6.3	5.27
Dunkeld (RI)	-22.71	1.86	2.94	Dunkeld (RI)	-16.35	3.61	4.96
CHANGES WITH FIELD EXPOSURE[1]							
Crossland Hill control	L	a	b	**Crossland Hill cleaned**	L	a	b
Glasgow (UI)	-11.46	-0.8	5.04	Glasgow (UI)	-9.44	-0.62	4.66
Aberdeen (UC)	-1.54	1.59	8.61	Aberdeen (UC)	-5.47	-0.53	3.85
Banff (RC)	-10.44	-0.06	5.19	Banff (RC)	-9.73	-1.18	3.08
Dunkeld (RI)	-9.88	-1.36	4.04	Dunkeld (RI)	-11.69	-1.75	5.78

Raw data in Appendix 8.7

[1] urban-coastal (UC); urban-inland (UI); rural-coastal (RC) and rural inland (RI).

In the Locharbriggs control (Figure 8.16a), the percentage change of the three colour components with location was significant for the brightness (L) and the other two chromacity components (a and b). Brightness decreased in all field sites, Dunkeld>Glasgow>Banff>Aberdeen. This means darkening of the stone surface on exposure is more important at inland sites. The components (a) and (b) increased in all field sites, especially at Aberdeen and Banff. These colour components have been interpreted as associated with the development of biological growths (Young, 1998), in particular a (green to red). A shift towards positive values indicate red dominance rather than green implying that there has been no green algal growth on these surfaces. Reddening of the surface can be explained by the weathering process.

The percentage changes for the Locharbriggs cleaned sandstone (Figure 8.16b), were also significant for all colour components (L, a, b). For all field sites, brightness decreased (darkening) and b increased (shift towards yellow). Colour component (a) increased significantly at the coastal sites (Aberdeen and Banff) compared to the samples exposed to the inland sites, especially Dunkeld. These changes followed approximately the same trend as the control samples and can be associated to the weathering process.

For the Crossland Hill control and cleaned samples (Figures 8.17a-b), brightness (L) and green-red (a) decreased and blue-yellow increased after exposure in all field sites. These results indicate a darkening of the stone surfaces and a shift towards green and therefore the possibility of resoiling probably related to biological growth.

After exposure brightness decreased in both sandstones and in all field sites, indicating possible darkening by resoiling of the surface. The colour components (a and b) increased for Lochabriggs, indicating shift towards red and yellow respectively, and (a) decreased for the Crossland Hill samples, indicating shift towards green. In the first case, changes are probably associated with the weathering process and in the second case with biological growth.

These results show that the changes in colour after 24 months exposure were independent of the cleaning regime applied to the stone. Also, they showed how location had a significant effect on the changes of the colour components, L, a and b. Similar results have been previously reported where cleaning of sandstone did not appear to have a major influence on the soiling of stone by algae (Urquhart *et al.,* 1995). These authors also indicate the important influence of geographical location on both the type of algal growth and on the growth intensity. In general, the east and north east of Scotland have significantly less precipitation than the west and south west and therefore more opportunities for algal growth. The average rainfall in the four sites selected (Section 3.8) indicate that both urban sites (Glasgow and Aberdeen) had a larger annual rainfall than the rural sites (Banff and Dunkeld) independently of east or west location. Therefore, other parameters must be considered to explain why Dunkeld (the site with less rainfall) had the largest shift towards green for Crossland Hill sandstone. A possible explanation could be a larger retention of moisture for a longer time.

Based only on colour changes, a coastal-urban setting will result in less darkening and less algal growth independently of the sandstone type and the cleaning regime.

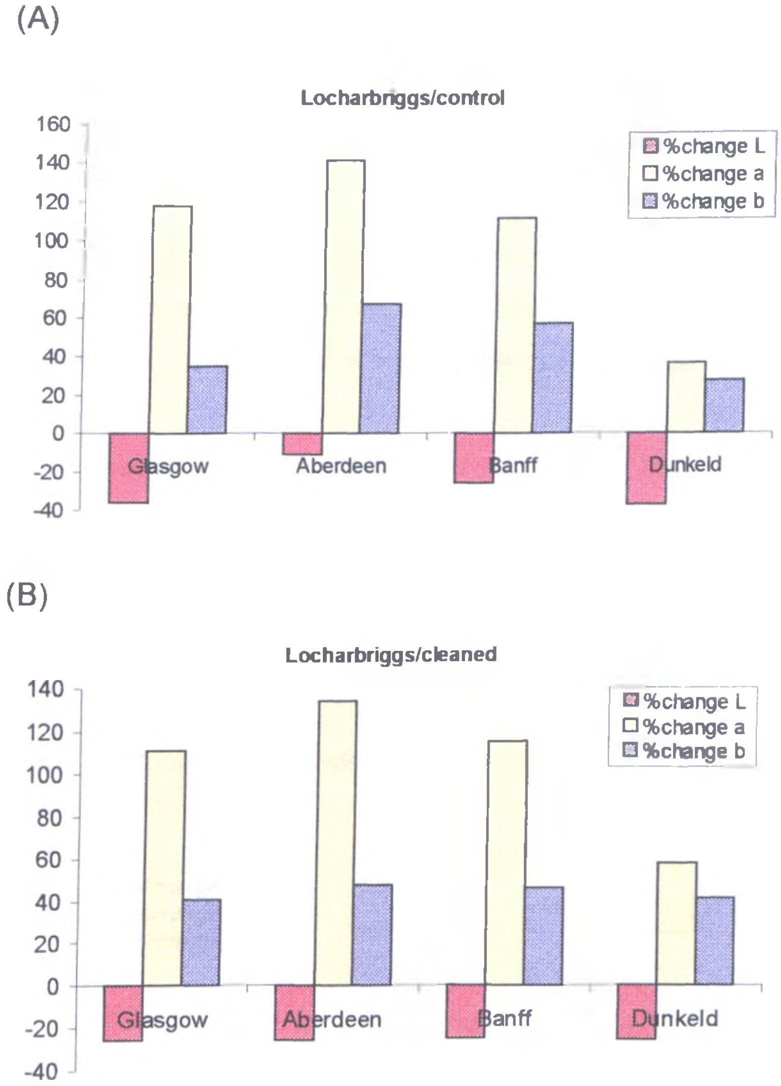


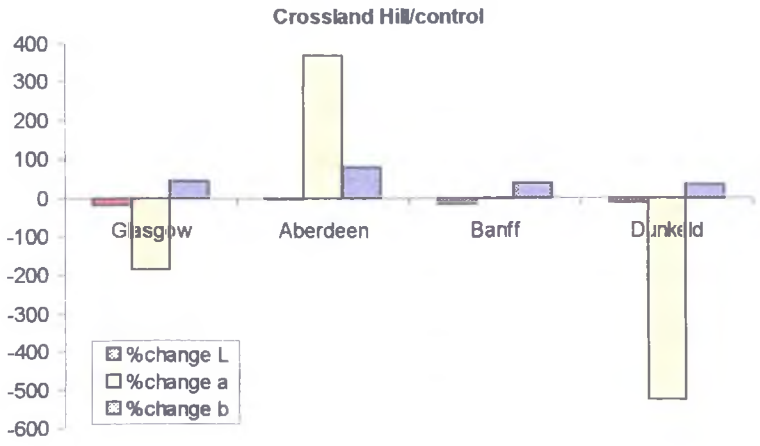
Figure 8.16a-b Colour percentage change for brightness (L) and colour components (a and b) with exposure.

The analysis of the percentage change in colour for the Crossland Hill control sandstone (Figure 8.17a) showed significant differences in the component (a) with location. The values for a (green to red) decreased at all sites, but Aberdeen, indicating a shift towards green and therefore the possibility of biological growth. In this case, the decrease was more important at the two inland locations (Glasgow and Dunkeld).

The Crossland Hill cleaned samples followed similar trends to the control samples for the colour components, L and b (Figure 8.17b). The most interesting finding was associated to the changes in a (green to red). Although in all the field sites, there was a decrease and therefore a shift towards green, there was a clear distinction between urban (Glasgow and Aberdeen) and rural locations (Banff and Dunkeld). The changes were more important at the two rural site.

When comparing the control and cleaned surfaces, it can be concluded that cleaned surfaces exposed at rural locations (Dunkeld and Banff) will decrease the value a (green to red) more rapidly than urban locations (Glasgow and Aberdeen). Therefore, chemical cleaning had an effect on the development of resoiling and this effect was different depending on the location.

(A)



(B)

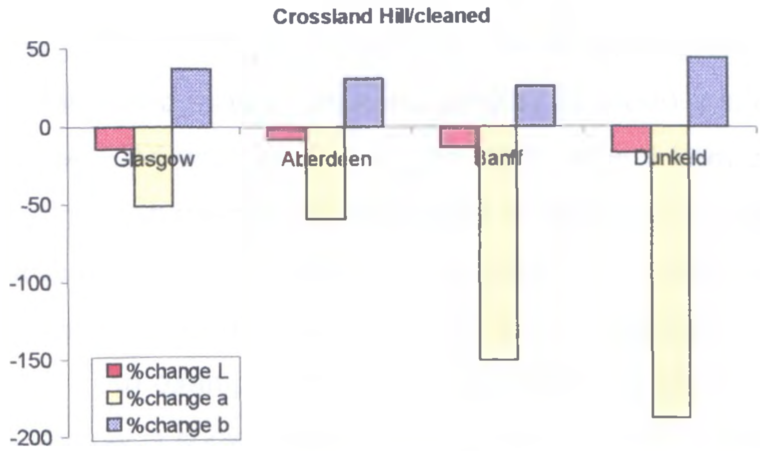


Figure 8.17a-b Colour percentage change for brightness (L) and colour components (a and b) with exposure.

8.5 Scanning Electron Microscopy

This technique enabled examination of the surface of the stone at a very small scale and across areas of few microns (Section 3.4). Small samples of control and chemically cleaned sandstones were coated with a thin layer of Au/Pd prior to examination.

Additionally, elemental map analysis and EDX analysis were performed on some of the selected images to obtain further qualitative information on the main elements present on the surface selected.

All the samples had been exposed for 24 months at the field sites (Glasgow, Aberdeen, Banff and Dunkeld) prior to analysis. Any significant difference between sites regarding elemental distribution can only be considered as a trend. In general, the samples presented a very irregular surface. This will clearly affect the intensity of the interactions between the beam and the minerals and therefore the number of x-rays detected from a particular element. Nevertheless, it was interesting to have a map of the elements to, for example, confirm the presence of potassium and iron. Both ions are very mobile and can be indicators of a weathering process.

For the Locharbriggs sandstones, control samples exposed at Glasgow (Plate 8.1a) presented a clean surface. The EDX analysis showed peaks for Si, Al, K, Ca and Fe (Appendix 8.8). The elemental map analysis clearly showed the presence of potassium from the feldspar grains, the iron deposit and the calcium and sulphur localised patches between grains. The presence of sulphur in the EDX was masked by the strong signal from gold used as coating agent but nevertheless its presence was clearly observed after mapping. Calcium was probably present as an initial component of Locharbriggs sandstone most likely originated from the mortar or from the atmosphere.

An example of Locharbriggs chemical cleaned samples also exposed at Glasgow is shown in Plate 8.1b. The EDX analysis showed peaks for Si, Al and K (Appendix 8.8). The elemental map analysis indicated the presence of some sulphur residues between mineral grains. This sulphur appeared in combination with calcium and here as in the control samples it is strongly suggestive of the presence of calcium sulphate, a known soiling agent.

After exposure in Aberdeen both control and clean samples presented a similar element map/SEM image (Plate 8.2a-b). EDX confirmed the presence of Si, Al, K and Fe (Appendix 8.8).

For the Crossland Hill sandstone, examples of chemically cleaned samples exposed at Glasgow and Banff are shown. In Glasgow (Plate 8.3a-b), some quartz grains appeared very decayed and in general iron-bearing minerals surrounded the mineral grains and intergranular space. EDX analysis confirmed the important contribution of Fe together with Si, Al and K mainly. The cleaned sample in Banff presented cleaned quartz grains with little debris on the surface (Plate 8.4a-b). EDX confirmed the presence of Si, Al, Fe, K, Cl and Na and elemental map analysis indicated the distribution of these elements (Appendix 8.8). Potassium at the mica and feldspar minerals, iron as cementing material between grain minerals or at the surface of quartz grains, sodium and chloride appeared together and this was an indication of proximity to the coast.

Plate 8.1a-b SEM photomicrograph showing the appearance of the Locharbriggs control (A) and chemically cleaned (B) surfaces after exposure in Glasgow (UI)

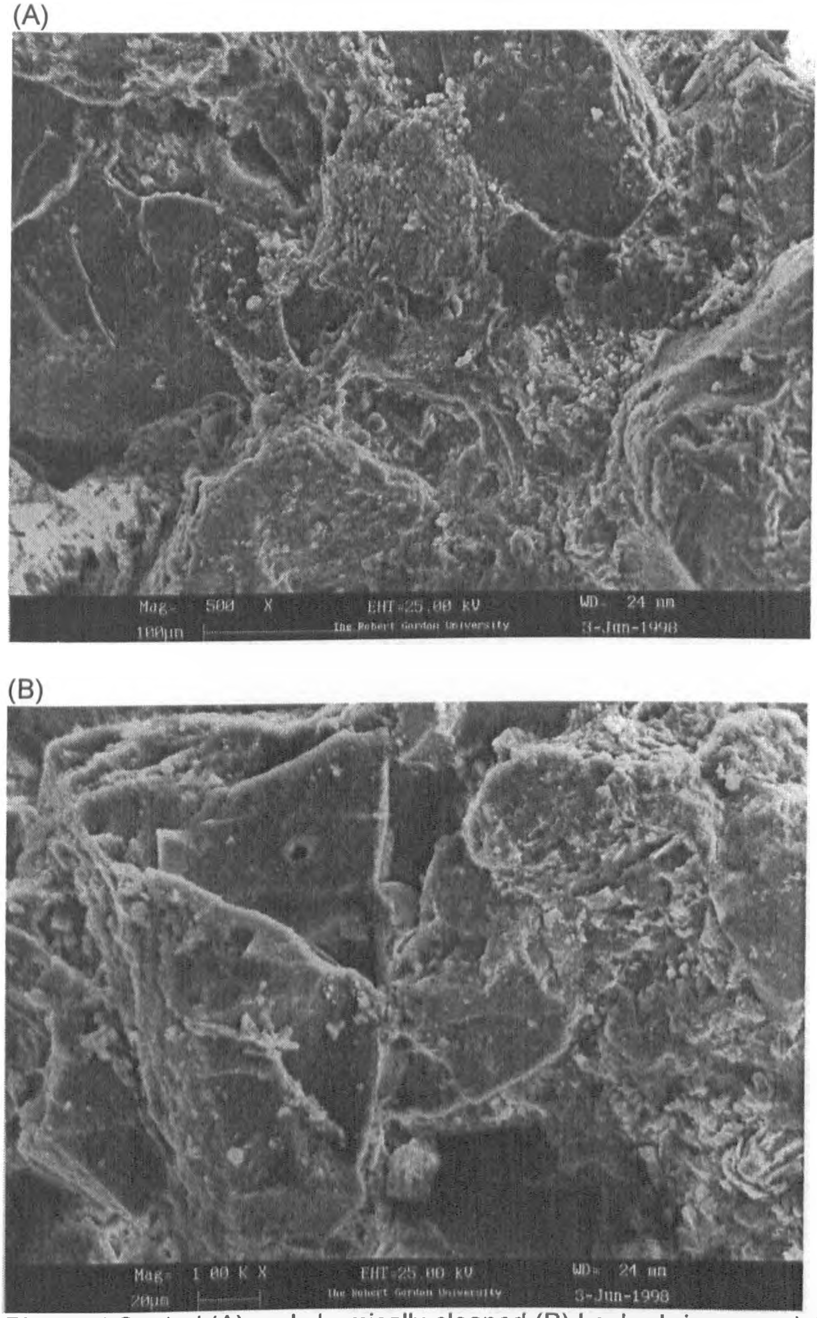


Plate 8.1 Control (A) and chemically cleaned (B) Locharbriggs sandstones after exposure in Glasgow.

Plate 8.2a-b SEM photomicrograph showing the appearance of the Locharbriggs control (A) and chemically cleaned (B) surfaces after exposure in Aberdeen (UC)

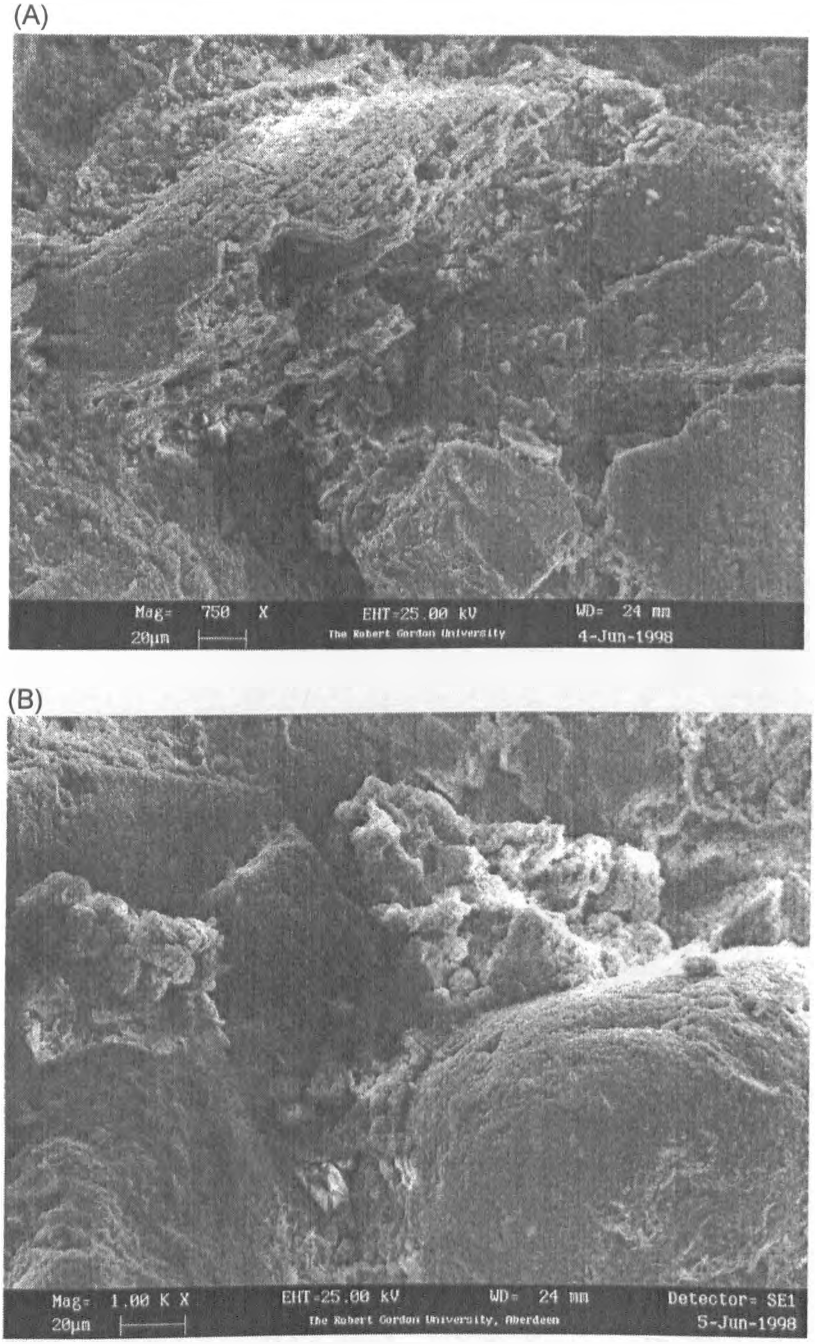


Plate 8.3a-b SEM photomicrograph showing some decayed quartz grains (A) and accumulated soiling between grains (B) of cleaned Crossland Hill surfaces after exposure in Glasgow (UI)

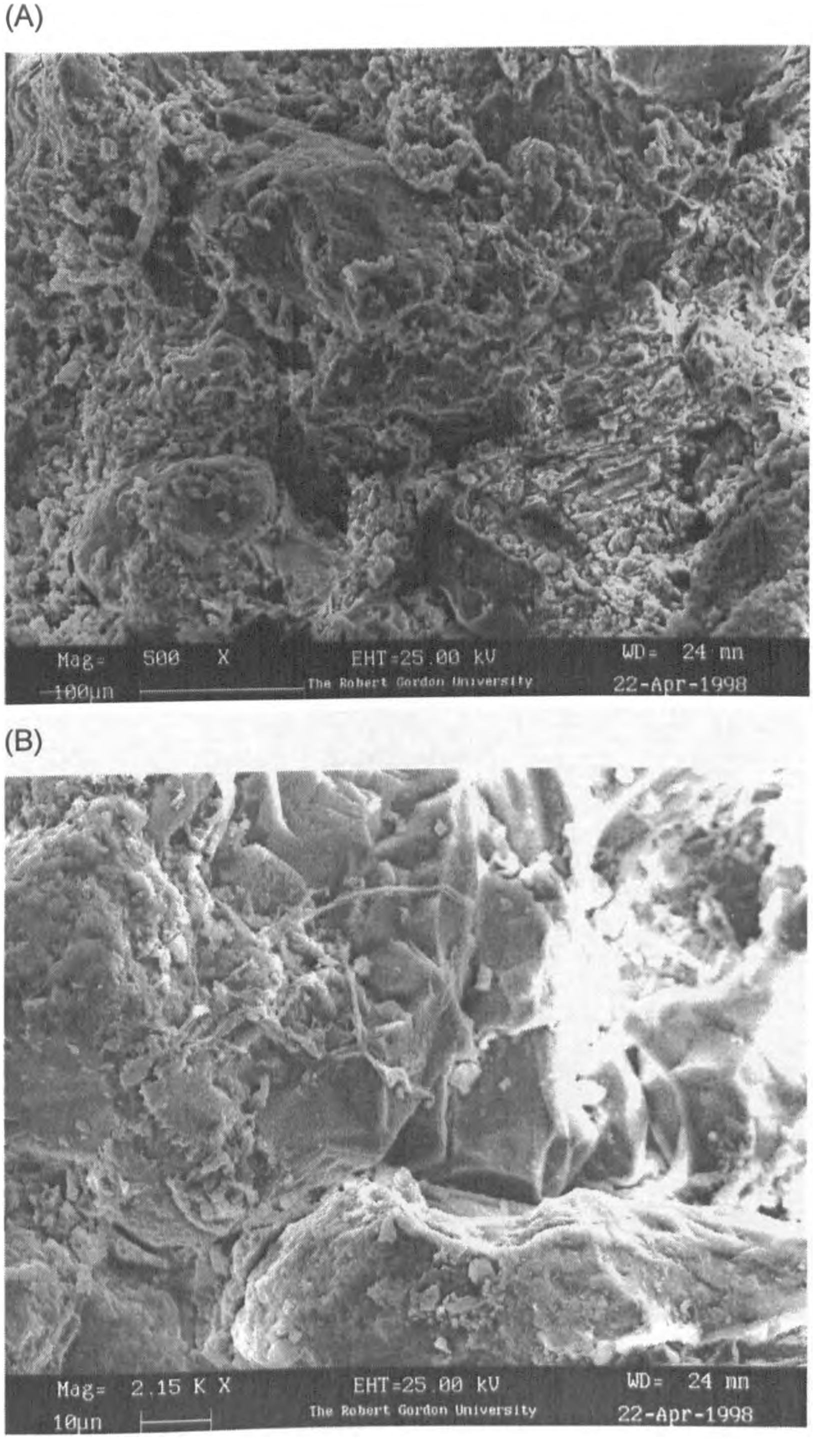
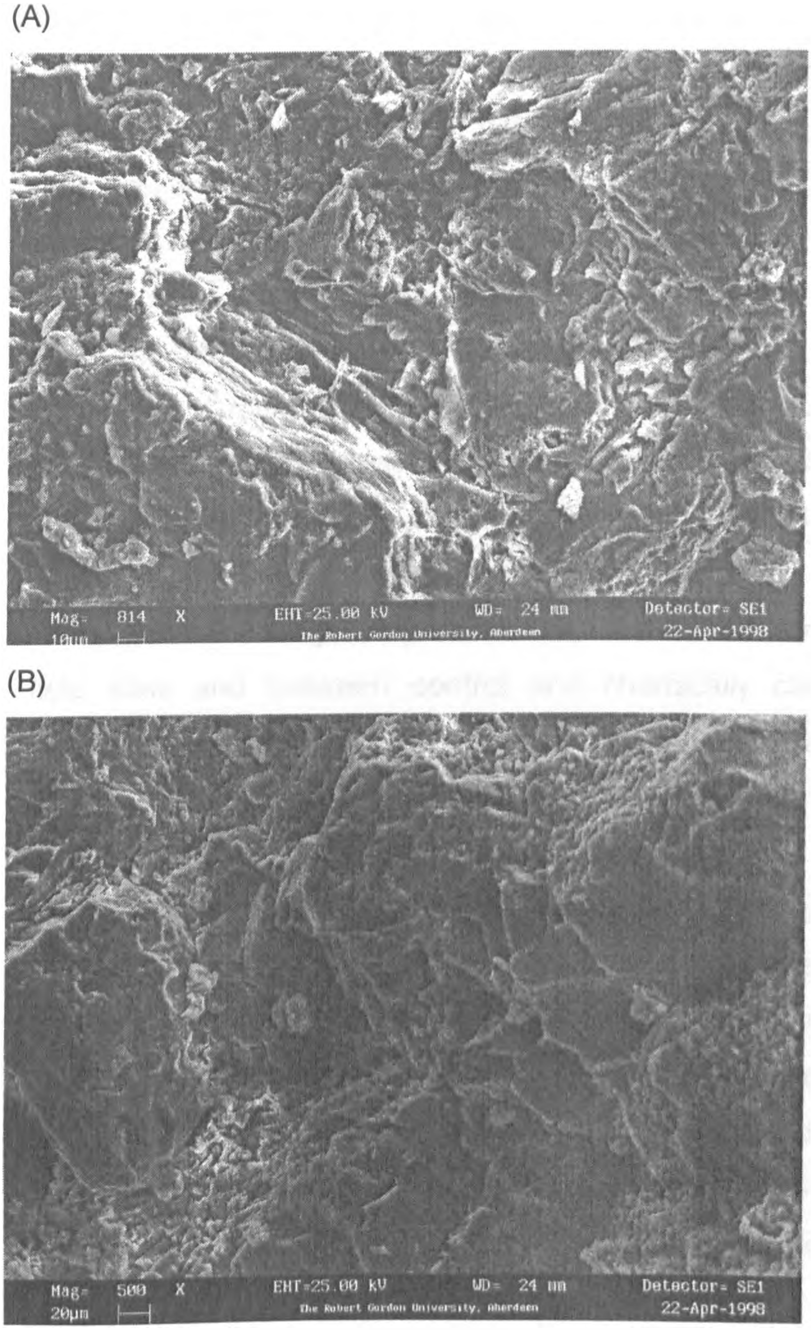


Plate 8.4a-b SEM photomicrograph showing the typical appearance of mica (A) and potassium feldspar (B) of cleaned Crossland Hill surfaces after exposure in Banff (RC)



8.6 Conclusions

Field exposure of the sandstones showed that overall porosity and porosity distribution will change in accordance to the type of sandstone involved and the reactions between the component minerals and the environment. The differences between both sandstones lie predominantly on their content of clay, mica and orthoclase feldspar. The dissolution of mica is thermodynamically preferred (Section 1.4). Micas will release potassium and magnesium ions which precipitate in combination with fluoride (post-cleaning residue), nitrate or sulphate (atmospheric pollution). This would explain the results for Crossland Hill cleaned sandstone. Assuming the dissolution of kaolinite takes place then the expected weathering product would be a mix of silicic acid (H_6SiO_4) and aluminium hydroxide $Al(OH)_3$ which would probably block the pore space of the Locharbriggs sandstone.

But mineralogy only cannot explain the differences in porosity between field sites and between control and chemically cleaned samples. For the Locharbriggs sandstone, the loss in porosity was largest at rural settings and for control samples. For the Crossland Hill sample, the loss was also largest at rural settings but for the cleaned samples.

As described in Section 8.1, the initial porosity of the control Locharbriggs and the cleaned Crossland Hill samples is larger than for the cleaned Locharbriggs and control Crossland Hill respectively. This initial larger porosity implies more water available in the pore network. This water must play an important role in the way soluble residues distribute and redeposit within the stone with the final effect of a larger decrease of porosity.

The four locations selected in the studies presented variations in rainfall levels, temperature and gale wind (Section 3.10). The pollution levels are only known for the Aberdeen site (urban-coastal) and they indicate larger levels of NO_2 (127 µg/m^3) compared to SO_2 (20 µg/m^3). Both gases are well below the EU recommended level set at 200 µg/m^3 and 100 µg/m^3 respectively. These variables probably play an important role on the porosity distribution differences found between field sites. It is known that variations on temperature and amount of water (rainfall) contribute to differences on the salt weathering processes. Additionally, differences between solubilities and crystal growth behaviours of different salts will result in crystallisation in the pore network of the stone and reduction of porosity. Both rural set-ups, Banff and Dunkeld, presented a lower average yearly rainfall when compared to the urban sites, Glasgow and Aberdeen. Also the daily mean temperature was lower.

Both sandstones contain soluble and insoluble salts which are the weathering product of mineral components (aluminium and silicon forms), the results of the cleaning process (sodium and fluoride salts) or previous natural exposure (calcium from the mortar, sulphates and nitrates from polluted environments, chlorides from coastal locations). As stone weathers, chemical displacement reactions may occur as suggested by Spry (1990). These reactions will involve conversion of one class of salt into another one which can be more damaging to the stone. This would imply that the type of salt that is present in the stone may determine the degree of salt weathering. This could also translate into differences in porosity and pore size distribution for the same stone at different locations. The selected soluble ions would be an indicator of this variability and therefore of potential salt weathering.

For the Locharbriggs samples, the only significant differences between field sites were found for nitrate (higher in Aberdeen) and chloride (higher at coastal sites). For the Crossland Hill, magnesium varied significantly with location and the percentage change was always higher at the rural sites.

When comparing control and cleaned samples, the only differences were found in potassium for the Locharbriggs samples and nitrate for the Crossland Hill samples.

Crossland Hill sandstone has a significant content of orthoclase feldspar and mica compared to Locharbriggs. The possibility of dissolution reaction of these aluminosilicates would result in the release of silica, aluminium, potassium and magnesium cations. On the other hand, Locharbriggs has more clay and dissolution of these clays would explain the leaching of potassium and magnesium in this sandstone. These products of reaction if deposit as non-crystalline aluminium and silicon forms can probably contribute to a reduction of pore space. There are evidences to suggest these type of precipitation reactions will take place in acidic conditions (Wilson, 1987).

Scanning electron microscopy allowed examination of surfaces after exposure. Comparison of Locharbriggs control and cleaned sample correlate well with the porosity results. These showed a larger reduction for the control samples. Comparison of Crossland Hill samples at different locations indicated the presence of some biological growth on the surface.

Colour changes indicated a decrease in brightness for both sandstones and in all field sites regardless the initial cleaning applied. These changes are probably associated to the weathering process. The colour component (a) increased for Lochabriggs, indicating a reddening of the surface, and decreased for the Crossland Hill samples, indicating shift towards green and possible algal growth. Visual observation of the samples by optical microscopy also confirmed these observations.

Finally, a summary of the results in this chapter is shown in Figure 8.18.

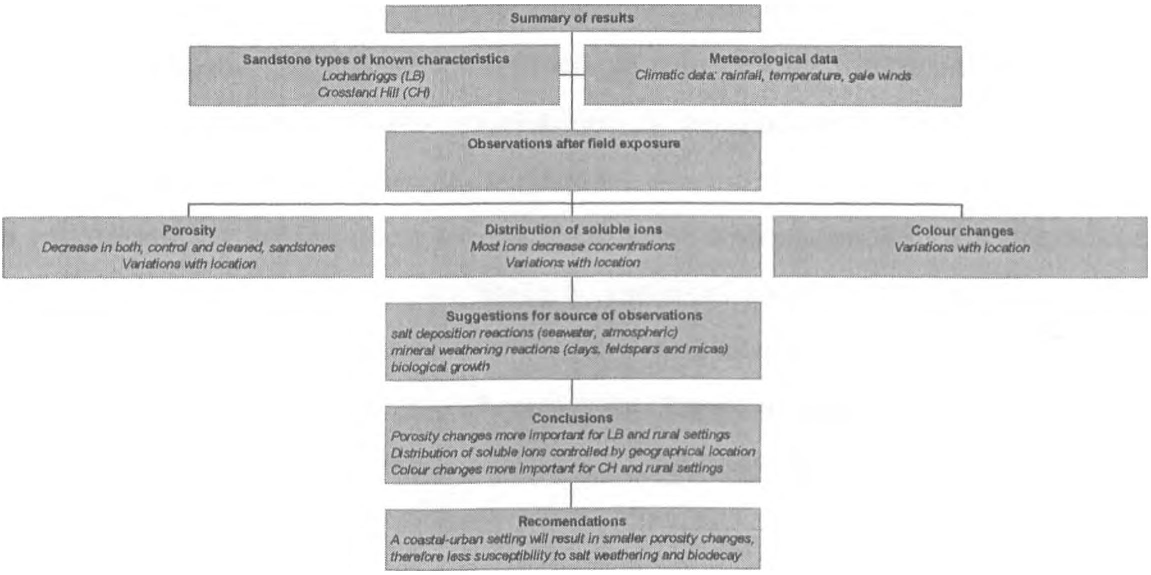


Figure 8.18 Summary of results after the field exposure studies.

9 CONCLUSIONS

In a global perspective, three different inter-related factors seem to explain the differences in salt-induced weathering of building sandstone. These three factors have been identified as: sandstone type, cleaning regime and geographical location. Their effect was monitored by looking at the variations on a series of weathering indicators. These indicators were the porosity, the distribution of soluble ions in the stone and the colour changes. Finally, a classification on the importance of each factor is proposed.

The objectives of this project as described in Section 1 were:

- to relate the susceptibility of the sandstone to cleaning products retention to their mineralogical composition and/or physico-chemical properties (e.g. grain size, porosity, colour).
- to investigate the effects of chemical cleaning processes in the formation of damaging salts by using artificial weathering conditions.
- to investigate the impact of location at four different sites in Scotland in terms of porosity changes, mobilisation or development of salts and colour changes on chemical-cleaned surfaces.
- to determine indicators of the decay process associated with the interaction of chemical-cleaned sandstones (e.g. chemical composition, colour) and the environment (e.g. temperature, rain, wind and SO_2 gas).
- to investigate the possibility of synergism between weathering mechanisms (result of sandstone type, chemical cleaning and location) by using theoretical dissolution reactions.

9.1 Effects of sandstone mineralogy, cleaning regime and location on porosity and pore size distributions

Locharbriggs and Crossland Hill sandstones are both quartz arenites which mainly differ in their clay, mica and feldspar content. The mineralogy of Locharbriggs is characterised by the presence of clays (illite and smectite-kaolinite clays, 2%) as well as feldspars (7%) and micas (1%) while the Crossland Hill is characterised by having more feldspars (12%) and micas (6%) and only traces of clays.

Chemical cleaning had an effect in the porosity distribution of the two sandstones (Chapter 5). Both sandstones increased their porosity between 200-500 μm after chemical cleaning although Locharbriggs decreased significantly at the pore size between 10-80 μm and Crossland Hill remained unchanged at the characteristic pore size between 0.1-1 μm. This means that deposition of post-cleaning residues or resulting mineral-weathering products took place selectively at the pore region between 10-80 μm only and potential damage to the stone due to crystallisation of these secondary salts will occur at this level.

The effects of the selected cleaning regime on the dissolution reactions of the aluminosilicate minerals, was theoretically calculated in terms of standard free energy change and the equilibrium constants (Section 4.4). The results show how these reactions proceed in all cases with the preferential release of aluminium, potassium and sodium cations which in combination with available anions such as fluoride or hydroxy can result in the precipitation of secondary salts in the pore network (Table 9.1).

Table 9.1 Free energy change (ΔG^0) and equilibrium constant (K) values were calculated at 1at pressure and 25°C for a feldspar ($KAlSi_3O_8$), a mica ($KAl_3Si_3O_{10}(OH)_2$) and kaolinite clay ($Al_2Si_2O_5(OH)_4$).

Reaction equilibrium	**ΔG^0 kJ/mol**	**Equilibrium constant, K (25°C)**
$KAlSi_3O_8$ (s) +22HF (l) $\xleftrightarrow{H_2O}$ $3H_2SiF_6$ (s)+ AlF_3 (s)+ KF (s) + 8 H_2O	-276.3	10^{48}
2 $KAl_3Si_3O_{10}(OH)_2$ (s)+ 2HF $\xleftrightarrow{H_2O}$ 3 $Al_2Si_2O_5(OH)_4$ + 2KF (s)+ H_2O	-954.4	10^{167}
$Al_2Si_2O_5(OH)_4$ (s)+ 18HF $\xleftrightarrow{H_2O}$ $2H_2SiF_6$ (s)+ 2 AlF_3 + 9 H_2O	-396.9	10^{70}
$KAlSi_3O_8$ + 22 H_2O $\xleftrightarrow{H_2O}$ $4K^+$ + $4OH^-$ + 8 H_4SiO_4 (s)+$Al_4[Si_4O_{10}](OH)_8$	-10807.7	10^{1893}

The same cleaning process had opposite effects on the two sandstones selected and therefore it can be concluded that sandstone type or mineralogy of the stone is the main factor controlling the porosity changes observed after chemical cleaning. A larger clay content in this case will translate into a greater tendency to weathering and deposition of the resulting products in the pore network.

The chemically cleaned samples were selected for further investigation of the porosity and pore size distribution after partial immersion in deionised water and contaminated salt-systems (Chapter 6). The Locharbriggs samples showed an increase in the overall porosity in both the free and the salt-contaminated systems. These changes took place mainly at the pore size between 10-80 µm. On the other hand, the Crossland Hill samples decreased the overall porosity in all solutions and the most affected pore size was between 100-500 µm.

These results recognised the effects of unsaturated salt systems at constant temperature. In the Locharbriggs sandstone, the proposed mechanisms imply an irreversible change in the grain-to-grain distance as a consequence of dissolution and deposition of salts at the near-surface. The presence of efflorescences on the Locharbriggs samples confirmed this hypothesis. In the Crossland Hill sandstone, precipitation reactions took place within the pore system. Preferential crystallisation was located in the larger pores (100-500 µm). These results agree with the thermodynamic model proposed by Wellman and Wilson (1965) who concluded that salt crystallisation takes place initially in the larger pores from solution being supplied from the smaller capillaries.

When similar salt-contaminated samples were exposed to cyclical weathering of humidity and temperature (Chapter 7), the porosity and pore size distribution also changed similarly to the samples partially immersed at constant temperature. The results showed an increase in overall porosity for Locharbriggs, mainly between 20-50 µm, although there were not significant changes for the Crossland Hill samples. The mechanism proposed also involved change in grain-to-grain distances which result in smaller distances during the wetting cycle than during the drying cycle and the development of a dilatation which results in an irreversible change, expansion in this case. SEM confirmed these observations in the Locharbriggs sandstone and showed that the differences in porosity distribution reflect the differences in actual pore size. Actual pore sizes appear to lie mostly within the 50-100 µm diameter range. The Crossland Hill sandstone, on the other hand, did not show a well developed system of pores.

The overall effect after natural exposure at four different locations was a reduction in porosity. For the Locharbriggs sandstone, the loss in porosity was largest at rural settings (Dunkeld and Banff) and for the control (not cleaned) samples. For the Crossland Hill sandstones, the loss was also largest at rural settings but only for the cleaned samples. Here, variations in mineralogy only cannot explain these differences. An initial larger porosity for the control Locharbriggs and the cleaned Crossland Hill samples respectively implies more water available in the pore network. This water must play an important role in the way soluble residues distribute and redeposit within the stone with the final effect of a larger decrease of porosity.

Both, Banff and Dunkeld, presented a lower average yearly rainfall when compared to the urban sites, Glasgow and Aberdeen (Section 3.8). The amount of rain will play an important role on the possible displacement reactions of soluble salts (e.g. $NaCl$ and Na_2SO_4) within the stone and in the location of these salts when they crystallise. It can be assumed that crystallisation processes took place more often at the rural sites and in the sandstones with an initial larger porosity. This could explain a much better predisposition to accommodate salts in agreement with the crystallisation theories that state how salts would start filling in the coarse porosity of both sandstones followed by the smaller pores. Additionally, chemical cleaning and atmospheric pollutants may contribute to biological regrowth and further porosity changes (Young, 1998).

Summarising the parallel experimental approaches it was found that for the controlled laboratory experiments, partial immersion or cyclical weathering of salt-contaminated samples resulted in the increase of porosity for Locharbriggs samples and a decrease or no significant change for the Crossland Hill samples. For the field studies, exposure resulted in a reduction in porosity in all cases.

In conclusion and based on the previous observations an order of importance can be established among the three factors, sandstone mineralogy, cleaning regime and geographical location and their effect on the porosity changes. This order would indicate that location is the most important factor followed by sandstone type and finally the cleaning regime.

9.2 Effects of sandstone mineralogy, cleaning regime and location on the distribution of soluble ions with depth

The cleaning method left soluble residues behind, mainly sodium and fluoride. Although these levels tend to decrease with depth, there were still present at depths of 20 mm (Figure 5.2a-b). Cleaning also had an effect on the release of ions such as potassium which can only have their origin in the mineral components. Potassium is released from feldspars and clays, especially at the near-surface which is subject to greatest attack by the cleaning agents. The proposed dissolution reaction for a feldspar and kaolinite are summarised in the previous section. Chemical cleaning therefore resulted in the introduction of sodium and fluoride ions in the stone and in the weathering of aluminosilicate minerals.

When sandstone samples were artificially exposed to SO_2 gas, both control and cleaned, samples increased the sulphate levels although the amount of sulphate found on chemically cleaned Locharbriggs and Crossland Hill sandstones was larger. The unrealistic concentration of SO_2 gas used in the experiment when compared to the levels found in Scotland probably influenced the findings. A continuous flow of 10 ppm SO_2 for 10 days has been reported to develop into gypsum crust on a calcareous stone (Mangio *et al.*, 1991) but in the case of siliceous sandstones the overall effect was simple adsorption and conversion into sulphuric acid. The important point is that the cleaning regime is the controlling factor on the adsortion and further conversion of SO_2 into sulphuric acid. These results would also suggest that cleaning of sandstone buildings located at urban sites could result in a more rapid weathering and decay through sulphuric acid attack.

The changes observed after field exposure indicated that, in general, independently of having a control (not cleaned) or a chemically cleaned sample, most ions decreased their concentration after exposure and presented a similar distribution pattern for all field sites. These results imply that excessive concentrations of post-cleaning residues in the sandstone samples prior to exposure do not play such an important role in the long-term because the natural weathering of the samples induce the stone to reach a balance so that control and cleaned samples reach a similar distribution profile.

Application of the principal component and discriminant analysis to the initial data matrix allowed the classification of the observations (soluble ions and climatic values) into three main factors which explained over 80% of the total variance: mineralogy, climatic and salt-load. The first factor grouped mainly potassium and sodium (weathering products of mineral components); the second, all the climatic variables (rainfall, temperature and gale wind) and the third factor generally comprises a number of residual salts from previous natural exposure (sulphates and nitrates from polluted environments, chlorides from coastal locations). Discriminant analysis allowed for the classification of the soluble ions into four different groups which correspond with the four locations: urban-coastal (Aberdeen), urban-inland (Glasgow), rural-coastal (Banff) and rural-inland (Dunkeld). In general, there was a separation between urban and rural sites although it would be necessary to have a larger data matrix to validate these trends. The differences found related to the type of sandstone and not the cleaning regime imposed on the stone. This means that in the case of the Locharbriggs sandstone, the urban-rural factor is the only one controlling the distribution of observations as in the Crossland Hill, both, urban-rural and inland-coastal factors, equally control the distribution.

Therefore, from the previous observations on the effects of the selected factors on the distribution of soluble ions, it can be concluded that geographical location is also here the most important controlling factor followed by the sandstone type and finally the cleaning regime.

9.3 Effects of sandstone mineralogy, cleaning regime and location on colour changes

Data confirmed that changes in colour do occur on exposure and the variation is dependant on the location and the sandstone type. For example, in the Locharbriggs sandstone, colour component green to red (a) increased significantly at the coastal sites (Aberdeen and Banff) compared to the inland sites, whereas, in the Crossland Hill sandstone, decrease occurs and is more important at the inland sites (Dunkeld and Glasgow). Based only on colour changes, these results imply that location is a very important controlling factor of the weathering of sandstone and suggest that a coastal-urban setting will result in less darkening and less algal growth independently of the sandstone type and the cleaning regime.

9.4 Classification of weathering factors and future recommendations

The main factors influencing salt-induced weathering of building stone are summarised in Figure 9.1. Effects which have been investigated in this thesis are shown on a white background. The influence of each factor on these indicators is shown by coloured arrows (blue for sandstone type, grey for cleaning regime and white for geographical location). The two sandstone types selected in this thesis are shown in a red (Locharbriggs) and yellow (Crossland Hill) background. Sometimes geographical locations are referred as: UC (urban-coastal), UI (urban-inland), RC (rural-coastal) and RI (rural-inland).

From the results shown in this research, it can be concluded that salt-induced weathering of building sandstone can be monitored over relatively short periods of time. Although, there are many factors that are involved in the process, it is possible to propose three inter-related factors to explain most of the variation found in the observations. These factors are identified as: sandstone type, geographical location and chemical cleaning. The order of importance with respect to conservation of the building heritage can be established as: geographical location, sandstone type and chemical cleaning regime. This means that if the aim is to reduce salt-induced weathering of existing sandstone buildings then chemical cleaning can be safely applied at certain locations and for certain sandstone types. For example, chemical cleaning of quartz arenite sandstones of relatively high porosity would be more suitable at urban-coastal locations than rural-inland locations. Locharbriggs sandstone with 22% porosity and a mineralogy characterised by a low clay content and a very high percentage of quartz (91%) is a very resistant stone to salt-induced weathering processes. In the long-term, exposure of Locharbriggs sandstone after chemical cleaning resulted in siginificant changes in porosity and colour with location. The minimum these changes are the less damage to the stone. In this work, location was defined by its proximity to the sea and by its proximity to a urban or rural environment. Aberdeen, which was classified as an urban-coastal location, presented the best conditions for the exposure of Locharbriggs sandstone. Crossland Hill sandstone with 9% porosity and a mineralogy characterised by high percentage of quartz (77%) and more vulnarable aluminosilicates such as feldspars (12%) and micas (6%) was also a resistant stone to salt-induced weathering processes. In this case, the data seem to indicate that an urban location will result in less damage to the cleaned stone.

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The results from this work open a new perspective onto the field of stonecleaning as it makes use, for the first time, of proposed theoretical

Appendix 5.1 Porosity raw data for the control and cleaned samples

sample :	Crossland Hill	Chemically cleaned	*shape factor : 3*	
1 sample wt. :	14.1360		*Hg surface tension : 0.480 Nm-1*	
2 bulk density :	2.3042		*contact angle : 140*	
bulk sample volume (ml)	6.1349		*porosity (%) :*	12.53

Corrected data

Pressure (psi)	**Pressure (kPa)**	**Pore width (um)**	**Cumulative volume (mL g-1)**	**Incremental volume (mL g-1)**	**Differential volume (mL g-1 um-1)**	**Cumulative porosity (%)**
0.486001	3.35	329.188	0	0	0	0
0.580334	4.00	275.6785	0.012842885	0.012843	0.00024	2.959272
0.661501	4.56	241.8523	0.017135317	0.004292	0.000127	3.948339
0.787668	5.43	203.1128	0.018733899	0.001599	4.13E-05	4.316686
0.922835	6.36	173.3629	0.018949252	0.000215	7.24E-06	4.366308
1.088669	7.51	146.9548	0.019286426	0.000337	1.28E-05	4.444
1.305169	9.00	122.578	0.019545414	0.000259	1.06E-05	4.503676
1.50917	10.41	106.0085	0.019710338	0.000165	9.95E-06	4.541678
1.741837	12.01	91.84822	0.019836121	0.000126	8.88E-06	4.570662
2.092338	14.43	76.462	0.020013018	0.000177	1.15E-05	4.611422
2.381338	16.42	67.18244	0.02010707	9.41E-05	1.01E-05	4.633094
2.853672	19.68	56.06241	0.020242599	0.000136	1.22E-05	4.664323
3.313007	22.84	48.28947	0.020327687	8.51E-05	1.09E-05	4.683929
3.861008	26.62	41.43552	0.020400831	7.31E-05	1.07E-05	4.700783
4.507676	31.08	35.49109	0.020485943	8.51E-05	1.43E-05	4.720394
5.283344	36.43	30.28039	0.02056645	8.05E-05	1.55E-05	4.738945
6.199846	42.75	25.80402	0.02064254	7.61E-05	1.7E-05	4.756478
7.287348	50.25	21.95312	0.020711201	6.87E-05	1.78E-05	4.772298
8.481017	58.48	18.86319	0.020782139	7.09E-05	2.3E-05	4.788644
9.89452	68.22	16.16833	0.020852632	7.05E-05	2.62E-05	4.804887
11.566856	79.75	13.8306	0.020917994	6.54E-05	2.8E-05	4.819948
13.53586	93.33	11.8186	0.020989689	7.17E-05	3.56E-05	4.836468
15.864032	109.38	10.084	0.021066451	7.68E-05	4.43E-05	4.854156
18.571537	128.05	8.613757	0.021128547	6.21E-05	4.22E-05	4.868464
21.738211	149.88	7.358843	0.021192421	6.39E-05	5.09E-05	4.883182
24.924417	171.85	6.418022	0.021188268	-4.15E-06	-4.41E-06	4.882225
29.922535	206.32	5.345848	0.021217236	2.9E-05	2.7E-05	4.8889
34.919991	240.77	4.580677	0.021262593	4.54E-05	5.93E-05	4.899351
40.917263	282.12	3.909162	0.021306966	4.44E-05	6.61E-05	4.909575
48.247208	332.66	3.315138	0.021367965	6.1E-05	0.000103	4.923631
56.409821	388.95	2.835311	0.021440976	7.3E-05	0.000152	4.940454
64.90625	447.53	2.464052	0.021517966	7.7E-05	0.000207	4.958194
76.067078	524.48	2.102396	0.021624789	0.000107	0.000295	4.982808
89.893913	619.82	1.778894	0.021735858	0.000111	0.000343	5.008401
104.720093	722.05	1.526922	0.021866884	0.000131	0.00052	5.038592
122.879608	847.25	1.301147	0.021992148	0.000125	0.000555	5.067456
143.036865	986.24	1.117668	0.022171472	0.000179	0.000977	5.108776
167.025284	1151.64	0.957028	0.022378486	0.000207	0.001289	5.156476
197.341843	1360.67	0.809878	0.022679739	0.000301	0.002047	5.225891
229.987198	1585.76	0.694803	0.02306629	0.000387	0.003359	5.314961

269.120544	1855.59	0.59365	0.023666181	0.0006	0.005931	5.453188
314.899445	2171.23	0.507227	0.024655059	0.000989	0.011442	5.681047
367.140778	2531.44	0.434935	0.026312257	0.001657	0.022924	6.0629
429.14978	2958.99	0.37197	0.029152761	0.002841	0.045113	6.717412
502.745178	3466.43	0.317398	0.033446393	0.004294	0.078677	7.706756
589.72229	4066.14	0.270463	0.03686577	0.003419	0.072854	8.494653
688.608521	4747.96	0.231505	0.038921438	0.002056	0.052766	8.968322
809.373047	5580.63	0.196839	0.040175167	0.001254	0.036166	9.257208
947.155029	6530.63	0.168085	0.041121656	0.000946	0.032916	9.475299
1103.946411	7611.71	0.144095	0.041893696	0.000772	0.032181	9.653193
1289.904419	8893.89	0.123202	0.042684654	0.000791	0.037858	9.835447
1510.864258	10417.41	0.105063	0.043435167	0.000751	0.041376	10.00838
1768.323364	12192.59	0.089646	0.044207236	0.000772	0.050079	10.18628
2070.956299	14279.24	0.076425	0.044862988	0.000656	0.049599	10.33738
2425.08667	16720.97	0.065144	0.045561365	0.000698	0.061907	10.4983
2833.717041	19538.48	0.055631	0.046266398	0.000705	0.074111	10.66076
3317.011719	22870.80	0.047405	0.047031598	0.000765	0.093022	10.83707
3875.974609	26724.84	0.040449	0.047778845	0.000747	0.10743	11.00926
4538.269043	31291.37	0.034425	0.048572576	0.000794	0.131769	11.19215
5306.561035	36588.74	0.029321	0.049406872	0.000834	0.163461	11.38439
6211.019531	42824.98	0.024931	0.050274528	0.000868	0.19763	11.58431
7261.814453	50070.21	0.021204	0.051104061	0.00083	0.222557	11.77546
8519.112305	58739.28	0.017952	0.051903799	0.0008	0.245961	11.95973
9966.581055	68719.58	0.015225	0.052634439	0.000731	0.267887	12.12809
11666.55566	80440.90	0.012886	0.05331162	0.000677	0.289514	12.28412
13646.53516	94092.86	0.010896	0.053906963	0.000595	0.299219	12.4213
15982.85254	110201.77	0.009183	0.054480905	0.000574	0.334912	12.55355
18693.67188	128892.87	0.007731	0.05502429	0.000543	0.374346	12.67876
21879.32813	150857.97	0.006485	0.055562863	0.000539	0.432207	12.80286
25589.98828	176442.97	0.005425	0.05608457	0.000522	0.492037	12.92307
29937.31836	206417.81	0.004517	0.056575569	0.000491	0.540827	13.03621

Appendix 5.2 Analysis of soluble ions after depth profiling

DEPTH ANALYSIS (mol/kg)

stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	Depth/mm
bcontrol	148.69	94.49	2638	65.23	376.55	68.78	10.2	0-2
bcontrol	516.72	57	1151	65.23	700	64.34	10.2	2-5
bcontrol	371.04	46.31	453.8	65.23	1076.96	95.41	10.2	5-10
bcleaned	186.3	76.88	104.15	1418.82	1884	105.87	10.2	0-2
bcleaned	233.75	60.42	50.53	1128.74	1076.96	83.14	10.2	2-5
bcleaned	154	54.17	30.57	871.93	806.67	76.7	10.2	5-10
rcontrol	139.84	60.12	35.63	65.23	323.04	68.78	10.2	0-2
rcontrol	460.68	545.96	25.82	65.23	215.38	64.34	10.2	2-5
rcontrol	116.45	41.5	25.82	65.23	215.32	95.4	10.2	5-10
rcontrol	149.63	147.56	30.54	65.23	161.55	84.94	10.2	10-20
rcleaned	113.45	39.97	31.35	2444.9	2153.28	105.87	10.2	0-2
rcleaned	108.06	39.97	46.14	1190.65	1883.63	83.14	10.2	2-5
rcleaned	83.17	39.97	25.82	977.15	1077	76.7	10.2	5-10
rcleaned	79.04	39.97	25.82	332.21	538.58	68.78	10.2	10-20

CROSSLAND HILL, %CHANGE WITH CLEANING

DEPTH	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium
0-2mm	25.29	-18.64	-96.05	2075.10	400.33	53.93	<0.1
2-5mm	-54.76	6.00	-95.61	1630.40	53.85	29.22	<0.1
5-10mm	-58.50	16.97	-93.26	1236.70	-25.10	-19.61	<0.1

LOCHARBRIGGS, %CHANGE WITH CLEANING

DEPTH	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium
0-2mm	-18.87	-33.52	-12.01	3648.12	566.57	53.93	<0.1
2-5mm	-76.54	-92.68	78.70	1725.31	774.56	29.22	<0.1
5-10mm	-28.58	-3.69	0.00	1398.01	400.19	-19.60	<0.1
10-20mm	-47.18	-72.91	-15.46	409.29	233.38	-19.03	<0.1

r is Locharbriggs; b is Crossland Hill

Appendix 5.3 Analysis of soluble ions after leaching in water for 30 days.

LEACHING ANALYSIS (mg/L)

stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	Time/days
bcontrol	0.35	0.63	0.66	0.22	0.5	0.2	<0.1	<0.1
bcontrol	2.6	2.41	2.43	0.22	1.8	0.9	0.1	5
bcontrol	5.3	4.98	4.1	0.84	5.8	1.4	0.4	15
bcontrol	7.07	6.55	5.04	1.55	9.8	1.6	0.6	30
bcleaned	0.3	0.81	0.7	<0.1	1.5	0.2	<0.1	<0.1
bcleaned	1.45	2.84	2.47	<0.1	4.9	1.5	0.1	5
bcleaned	3.04	5.91	4.44	1.62	12.3	2.7	0.7	15
bcleaned	3.97	9.58	5.43	3.12	18.3	2.9	1	30
rcontrol	0.25	1.16	0.95	0.1	1.5	0.2	<0.1	<0.1
rcontrol	2.3	5.66	5.74	0.5	4.9	1.5	0.1	5
rcontrol	5.84	13.82	11.59	4.55	8.3	4.4	0.6	15
rcontrol	7.41	18.42	14.21	6.32	10.3	5.7	0.8	30
rcleaned	0.12	0.89	0.74	1.38	2.5	<0.1	<0.1	<0.1
rcleaned	1.57	6.66	3.35	5.03	9.5	1.6	0.2	5
rcleaned	14.33	13.33	7.54	10.17	23.5	5.1	2.3	15
rcleaned	16.37	17	8.74	18.3	37.5	8.1	4.3	30

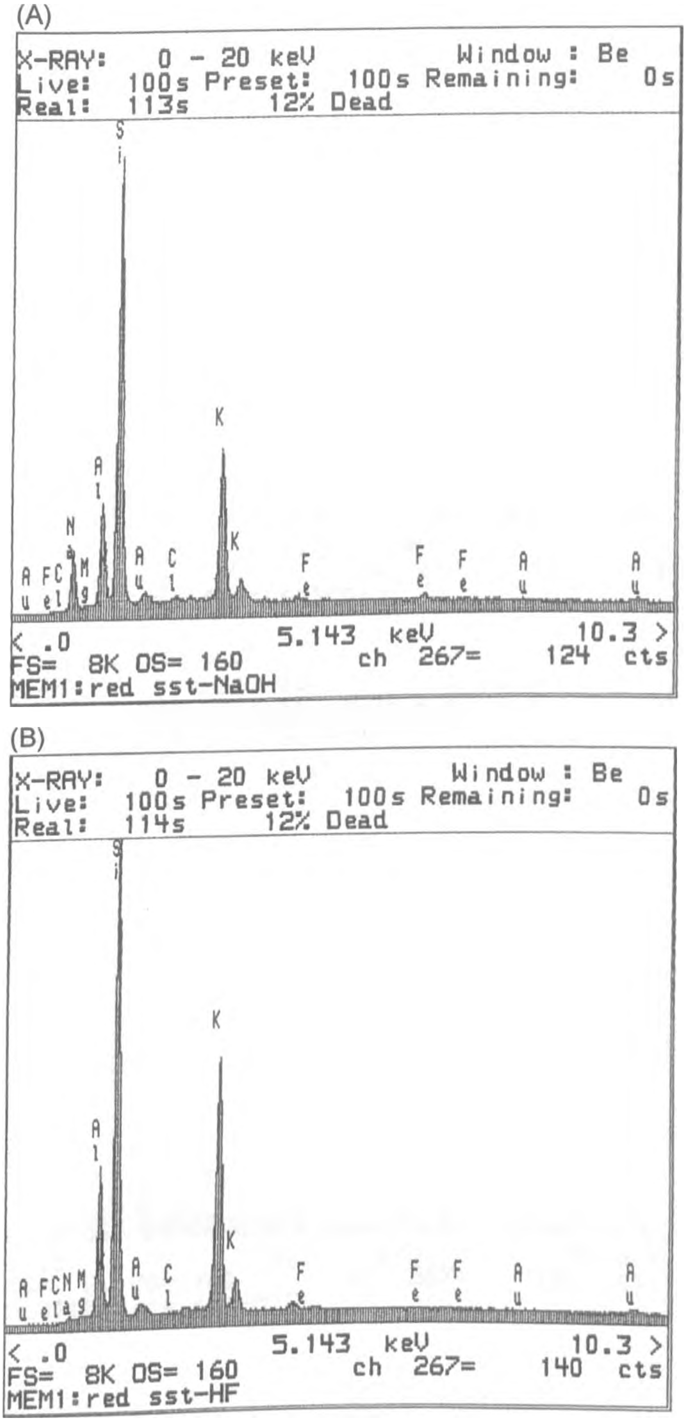
CROSSLAND HILL, %CHANGE WITH CLEANING							
Time/days	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium
0	-14	29	6	-100	200	0	0
5	-44	18	2	-100	172	67	0
15	-43	19	8	93	112	93	75
30	-44	46	8	101	87	81	67
LOCHARBRIGGS, %CHANGE WITH CLEANING							
Time/days	chloride	sulphate	nitrate	fluoride	sodium	potassium	Magnesium
0	-52	-23	-22	1280	67	-100	0
5	-32	18	-42	906	94	7	100
15	145	-4	-35	124	183	16	283
30	121	-8	-38	190	264	42	438

r is Locharbriggs; b is Crossland Hill

Appendix 5.4 Summary of the degrees of freedom and critical F value for the two sandstones

Source of variation	*Degrees of freedom*	
	Locharbriggs	**Crossland Hill**
Between sample	h –1 = 3	h – 1 = 2
Within sample	h(n – 1 = 4	h(n – 1) = 3
Critical value, F	$F_{3,4} = 6.591$	$F_{2,3} = 9.55$
P = 0.05		

Appendix 5.5 Results from the elemental dispersive X-ray analysis.



(A)

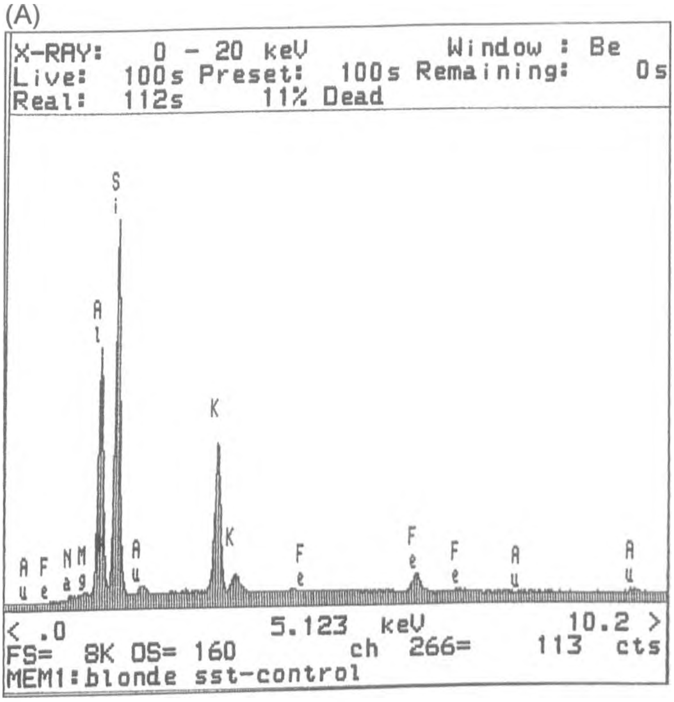
```
X-RAY:    0 - 20 keV          Window : Be
Live:   100s Preset:  100s Remaining:    0s
Real:   113s      12% Dead
< .0            5.143  keV          10.3 >
FS=  8K OS= 160      ch  267=     124  cts
MEM1:red sst-NaOH
```

(B)

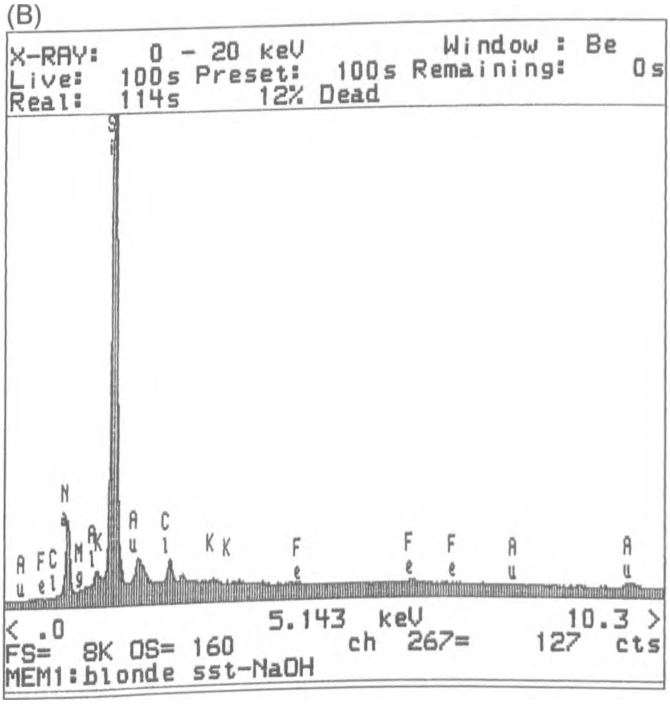
```
X-RAY:    0 - 20 keV          Window : Be
Live:   100s Preset:  100s Remaining:    0s
Real:   114s      12% Dead
< .0            5.143  keV          10.3 >
FS=  8K OS= 160      ch  267=     140  cts
MEM1:red sst-HF
```

EDX analysis of Locharbriggs sandstone after independent treatment with NaOH (A) and HF (B).

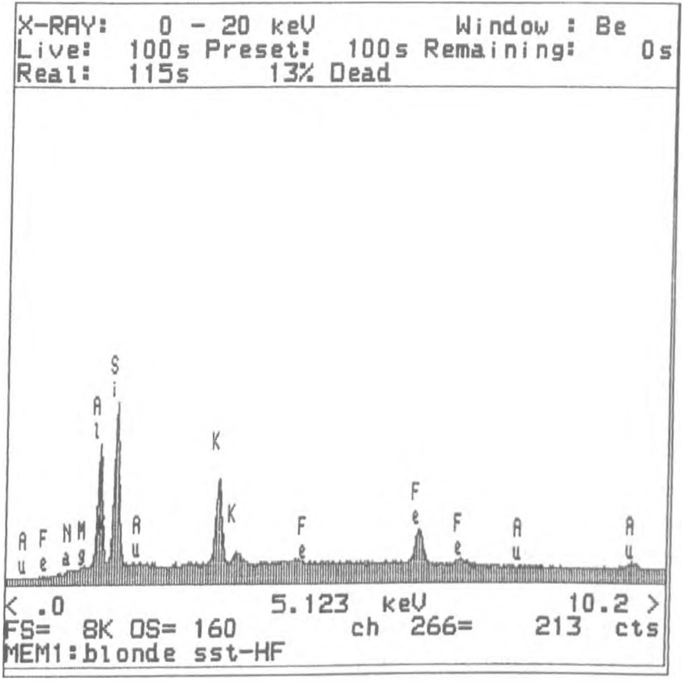
(A)


X-RAY: 0 - 20 keV Window : Be
Live: 100s Preset: 100s Remaining: 0s
Real: 112s 11% Dead
Si
Al
K
Au Fe Na Mg Au K Fe Fe Fe Au Au
< .0 5.123 keV 10.2 >
FS= 8K OS= 160 ch 266= 113 cts
MEM1:blonde sst-control

(B)


X-RAY: 0 - 20 keV Window : Be
Live: 100s Preset: 100s Remaining: 0s
Real: 114s 12% Dead
Si
Na
Au Fe Cl Mg Al K Au Cl K K Fe Fe Fe Au Au
< .0 5.143 keV 10.3 >
FS= 8K OS= 160 ch 267= 127 cts
MEM1:blonde sst-NaOH

(C)



```
X-RAY:    0 - 20 keV         Window : Be
Live:  100s Preset:  100s Remaining:    0s
Real:  115s       13% Dead
```

```
< .0              5.123  keV          10.2 >
FS=  8K OS= 160         ch  266=     213  cts
MEM1:blonde sst-HF
```

EDX analysis of Crossland Hill sandstone after independent treatment with water (A), NaOH (B) and HF (C).

Appendix 6.1 Raw data for the porosity of Locharbriggs and Crossland Hill sandstones.

Solution	**water**	**seawater**		**NaCl**	**Na_2SO_4**
Pore width (um)	Incremental volume (mL g-1) **water**	Incremental volume (mL g-1) **seawater**	Pore width (um)	Incremental volume (mL g-1) **NaCl**	Incremental volume (mL g-1) **Na_2SO_4**
284.2501	0	0	297.1866	0	0
251.8791	0.00068	0.00064	252.8077	0.004519	0.001871
227.3054	0.001099	0.000734	216.5375	0.004658	0.006408
204.106	0.000787	0.00082	193.1799	0.001558	0.001175
159.533	0.001416	0.001558	173.6764	0.00179	0.001413
147.792	0.000274	0.000296	144.6299	0.001644	0.001367
121.8466	0.000754	0.000739	123.334	0.001308	0.00091
110.3976	0.000357	0.000299	105.1953	0.00109	0.000806
89.16914	0.000656	0.000719	90.2252	0.001034	0.000715
77.41788	0.000455	0.000446	76.19496	0.001053	0.000715
65.07371	0.000636	0.000569	66.72014	0.000972	0.000634
55.90241	0.000642	0.000626	56.81229	0.001298	0.00081
48.74559	0.0008	0.000723	48.58275	0.001825	0.00099
41.53414	0.001356	0.001276	41.73459	0.002449	0.00154
35.51605	0.001644	0.002655	35.70896	0.003882	0.003654
30.39161	0.002775	0.007279	30.10753	0.007079	0.010564
25.91759	0.003474	0.008471	25.3381	0.009166	0.013709
22.17169	0.003652	0.009443	22.12568	0.007814	0.014849
18.94024	0.003233	0.01295	18.92493	0.00858	0.011304
16.07141	0.003628	0.010188	16.09243	0.009408	0.008793
13.828	0.005477	0.007552	13.78431	0.006646	0.006421
11.77972	0.007366	0.006161	11.82369	0.005062	0.004476
10.08305	0.004769	0.004247	10.09716	0.00408	0.003523
8.617469	0.003408	0.003132	8.612366	0.003193	0.002753
7.359013	0.00253	0.002383	7.3624	0.002357	0.002064
6.383447	0.001394	0.001233	6.426458	0.001405	0.001327
5.330642	0.001475	0.001629	5.328961	0.001608	0.0014
4.552183	0.001025	0.001045	4.571939	0.001208	0.00109
3.891056	0.000877	0.001043	3.905077	0.001041	0.000964
3.315213	0.000811	0.000946	3.348319	0.000954	0.000949
2.828112	0.000748	0.000858	2.852027	0.000917	0.000842
2.428187	0.000632	0.000841	2.458258	0.000821	0.000794
2.058869	0.000663	0.000787	2.094001	0.000815	0.000834
1.800329	0.000503	0.00074	1.803107	0.000694	0.000743
1.516088	0.000656	0.000776	1.525237	0.000723	0.000817

1.272814	0.000625	0.000678	1.312465	0.00059	0.000748
1.11721	0.000537	0.00081	1.115607	0.000798	0.000746
0.952949	0.000655	0.000796	0.955566	0.000791	0.000892
0.806307	0.000708	0.000863	0.814349	0.000837	0.000839
0.690183	0.000676	0.000819	0.693048	0.000938	0.000941
0.59391	0.000624	0.000898	0.592345	0.000902	0.000867
0.506289	0.00062	0.000812	0.507023	0.00081	0.000734
0.428517	0.00056	0.000678	0.435092	0.000687	0.00074
0.369987	0.000483	0.000685	0.369089	0.00063	0.000641
0.316229	0.000435	0.00059	0.317356	0.000616	0.000594
0.26817	0.000429	0.000551	0.270889	0.000524	0.000544
0.230789	0.000354	0.000467	0.231221	0.0005	0.000499
0.197365	0.000357	0.000458	0.197108	0.000438	0.000472
0.168641	0.000348	0.000445	0.169051	0.000399	0.000478
0.143951	0.000319	0.000405	0.144273	0.00041	0.000417
0.122664	0.000325	0.000408	0.122977	0.000369	0.000427
0.104819	0.000344	0.000375	0.105119	0.000376	0.000419
0.089679	0.000298	0.000335	0.089659	0.000337	0.00037
0.076256	0.000306	0.00033	0.076427	0.000307	0.000368
0.065183	0.000299	0.000314	0.065168	0.000297	0.000328
0.055652	0.000268	0.000294	0.055684	0.000278	0.000308
0.047376	0.000269	0.000281	0.047419	0.00027	0.000318
0.040461	0.000282	0.000277	0.040477	0.00031	0.000296
0.034424	0.00027	0.000265	0.034418	0.000255	0.000286
0.029331	0.000246	0.000278	0.029331	0.000243	0.00026
0.024917	0.000272	0.000229	0.024936	0.000244	0.000304
0.021162	0.000265	0.000247	0.02118	0.000252	0.000249
0.017949	0.000284	0.00024	0.017943	0.000245	0.000264
0.015222	0.000307	0.000256	0.015224	0.000238	0.000299
0.012893	0.000298	0.000218	0.012877	0.000252	0.00028
0.010899	0.000354	0.000228	0.010886	0.000213	0.000269
0.009188	0.000305	0.000259	0.009189	0.000247	0.000323
0.007735	0.000374	0.000258	0.007728	0.000202	0.000277
0.006483	0.000391	0.000308	0.006485	0.000223	0.000317
0.005421	0.000408	0.000291	0.005422	0.000257	0.000255

Solution	**water**	**seawater**		**NaCl**	**Na_2SO_4**
Pore width (um)	Incremental volume (mL g-1)	Incremental volume (mL g-1)	Pore width (um)	Incremental volume (mL g-1)	Incremental volume (mL g-1)
	water	**seawater**		**NaCl**	**Na_2SO_4**
317.0117	0	0	310.953	0	0
265.609	0.000332	0.000749	256.3181	0.000316	0.000304
232.3679	0.000287	0.001745	216.6841	0.000362	0.000409
202.6409	0.000277	0.000984	197.5124	0.000108	0.000107
165.9022	0.000377	0.001191	173.6451	0.000217	0.000213

147.3609	0.000212	0.000862	142.0194	0.000376	0.000425
123.7155	0.000277	0.000835	126.8546	0.000182	0.000174
105.705	0.000214	0.000509	104.8276	0.000255	0.000242
90.56567	0.000184	0.000265	91.00361	0.000136	0.000164
77.33058	0.000184	0.000305	77.56175	0.000194	0.000193
66.08624	0.000192	0.000321	65.42411	0.000166	0.000206
56.31235	0.000136	0.000183	57.09277	0.000155	9.46E-05
48.07422	0.000115	0.000159	47.73474	0.000148	0.000156
41.57372	0.000126	0.00013	41.18485	0.000161	0.000139
35.35645	0.000107	0.000153	35.50291	9.46E-05	9.47E-05
30.13305	0.000151	0.000132	30.2327	9.62E-05	0.000174
25.9309	0.000129	9.76E-05	25.79986	0.000106	0.00014
22.19219	0.000131	0.000119	22.13334	7.15E-05	6.24E-05
18.86505	0.000121	0.000145	18.58056	9.35E-05	0.000133
16.0954	0.000105	0.000109	16.12135	6.73E-05	8.39E-05
13.80791	8.57E-05	8.42E-05	13.78154	8.81E-05	7.2E-05
11.74053	0.000138	0.000113	11.78971	7.44E-05	0.00011
10.06792	9.2E-05	0.000104	10.08093	5.78E-05	6.85E-05
8.610588	0.000113	6.55E-05	8.615845	6.77E-05	6.97E-05
7.362796	0.000135	0.00012	7.351628	0.000109	0.000128
6.356753	2.09E-05	6.06E-06	6.310188	3.48E-05	9.03E-07
5.30322	5.28E-05	8.81E-05	5.270589	1.15E-05	6.65E-05
4.592841	8.61E-05	7.45E-05	4.482903	6.79E-05	6.89E-05
3.8396	8.75E-05	8.15E-05	3.900016	5.69E-05	5.08E-05
3.321434	0.000105	0.000106	3.285754	5.58E-05	9.89E-05
2.848304	0.000128	0.000138	2.855546	7.23E-05	6.79E-05
2.45486	0.000164	0.000117	2.441397	0.000111	7.39E-05
2.091075	0.000154	0.000135	2.113356	0.0001	0.000111
1.797291	0.000171	0.000153	1.793334	8.53E-05	0.000102
1.513676	0.000197	0.00026	1.438329	0.000171	0.000112
1.307342	0.000191	0.000353	1.279091	0.00011	0.00016
1.082919	0.00034	0.00033	1.093765	0.000167	0.000186
0.952699	0.000247	0.000406	0.903957	0.000197	0.000211
0.805381	0.000298	0.000552	0.802514	0.000204	0.00018
0.694974	0.000486	0.000782	0.696353	0.000358	0.000306
0.592269	0.000678	0.00113	0.586359	0.000606	0.000499
0.502457	0.001223	0.001665	0.501318	0.00104	0.000747
0.434491	0.001452	0.002655	0.430911	0.001855	0.001182
0.371565	0.002594	0.003918	0.369521	0.003224	0.002329
0.315851	0.003426	0.002942	0.318039	0.003876	0.002917
0.270583	0.002864	0.001833	0.270573	0.003584	0.003639
0.23208	0.002196	0.001134	0.230781	0.002412	0.002185
0.197124	0.001367	0.001026	0.196549	0.0014	0.001518
0.168407	0.00099	0.000919	0.168552	0.00104	0.001193
0.143935	0.000878	0.000911	0.143867	0.000969	0.000896
0.123019	0.000836	0.000814	0.122476	0.000894	0.000869
0.104963	0.0008	0.000835	0.104927	0.000883	0.000824

0.089777	0.000762	0.000906	0.089511	0.00088	0.000835
0.076395	0.000796	0.000785	0.076407	0.000891	0.000864
0.065172	0.000788	0.000827	0.065248	0.000885	0.000719
0.055571	0.000772	0.000871	0.055607	0.000926	0.000825
0.047385	0.000868	0.00093	0.047387	0.000988	0.000869
0.040465	0.000853	0.00093	0.040344	0.001026	0.000851
0.034427	0.000904	0.000962	0.03439	0.000971	0.000873
0.029314	0.000879	0.000913	0.029303	0.000939	0.000834
0.024923	0.000784	0.000802	0.024898	0.000849	0.000783
0.021178	0.000772	0.000762	0.02118	0.000775	0.000713
0.017946	0.000687	0.000673	0.017925	0.000697	0.000606
0.015219	0.000607	0.000613	0.01521	0.000628	0.000568
0.012884	0.000559	0.000547	0.01287	0.00058	0.000525
0.010889	0.000548	0.000554	0.010891	0.000502	0.000473
0.009184	0.00053	0.000503	0.009186	0.000526	0.00044
0.007728	0.000433	0.000521	0.007727	0.00046	0.000435
0.006486	0.000471	0.000487	0.006483	0.000515	0.000405
0.005421	0.000467	0.000504	0.005422	0.000467	0.000431

Appendix 6.2 Summary of experimental calculated tensile strength.

Locharb	weight/g	F(N)	*tensile(MPa)*	Crossland	F (N)	*tensile(MPa)*	weight/g
control	33.3084	3574	*1.14*	control	7440	*2.38*	33.0552
NaCl	30.29.97	5084	*1.62*	NaCl	7626	*2.44*	40.7254
Na2SO4	33.3943	4922	*1.57*	Na2SO4	7623	*2.42*	40.1879
seawater	32.7431	4900	*1.57*	seawater	7625	*2.4*	40.9951
Salt solutions: NaCl, 0.1M				salt	interfacial tension (N/m) theory		
	Na_2SO_4, 0.1M			NaCl	0.0728		
Dimensions: 20mm diameter *40mm high				Na_2SO_4	0.0727		
tensile = F/area			AREA = $0.785D^2$				

Sample	Porosity %	Class pore size				
LB	18.23	I	II	III	IV	V
CH	12.5	r < 0.1	0.1 < r < 1	1 < r < 10	10 < r < 100	r > 100
Locharbriggs		1	7	27	36	29
Crossland Hill		14	52	12	7	15

Appendix 6.3 Summary of theoretical calculated pressures.

Salt	*Sample: Locharbriggs/cleaned*						
NaCl	0.045 μm	0.45 μm	4.45 μm	45 μm	**Pt = 2σ (1/r - 1/R)**		
Vr/VR	0.1428	0.3571	2.9285	2.7142	interfacial tension = 0.0727 N/m		
Ptheory	3.196	0.318	0.0309	0.0024	**Pe = Pt *Vr/VR**		
Peffective	*0.45639*	*0.11356*	*0.09049*	*0.00651*	1/R = 0.005		
Ptotal =	**0.66695**						
Salt	*Sample: Locharbriggs/cleaned*						
Na_2SO_4	0.045 μm	0.45 μm	4.45 μm	45 μm	**Pt = 2σ (1/r - 1/R)**		
Vr/VR	0.1666	0.5833	3.25	3.33	interfacial tension = 0.0727 N/m		
Ptheory	3.196	0.318	0.0309	0.0024	**Pe = Pt *Vr/VR**		
Peffective	*0.53245*	*0.18549*	*0.10043*	*0.00799*	1/R = 0.005		
Ptotal =	**0.82636**						
Salt	*Sample: Crossland hill/cleaned*						
NaCl	0.045 μm	0.45 μm	4.45 μm	45 μm	**Pt = 2σ (1/r - 1/R)**		
Vr/VR	1.4375	2.625	0.4375	0.75	interfacial tension = 0.0727 N/m		
Ptheory	3.196	0.318	0.0309	0.0024	**Pe = Pt *Vr/VR**		
Peffective	*4.59425*	*0.83475*	*0.01352*	*0.0018*	1/R = 0.005		
Ptotal =	**5.44432**						
Salt	*Sample: Crossland hill/cleaned*						
Na_2SO_4	0.045 μm	0.45 μm	4.45 μm	45 μm	**Pt = 2σ (1/r - 1/R)**		
Vr/VR	1.666	2.66	0.6	0.733	interfacial tension = 0.0727 N/m		
Ptheory	3.196	0.318	0.0309	0.0024	**Pe = Pt *Vr/VR**		
Peffective	*5.32454*	*0.84588*	*0.01854*	*0.00176*	1/R = 0.005		
Ptotal =	**6.19072**						

Appendix 7.1 Depth analysis of soluble anions in Locharbriggs control and cleaned sandstone

DEPTH ANALYSIS (µg/g):LOCHARBRIGGS /BEFORE EXPOSURE

stone	chloride	nitrate	sulphate	Depth/mm
control	2.92	17.91	5.00	0-2
control	2.51	15.67	4.00	2-5
control	19.08	28.63	17.94	5-10
control	7.61	18.81	5.00	10-20
cleaned	7.60	33.57	2.50	0-2
cleaned	2.92	24.15	2.50	2-5
cleaned	6.25	35.35	2.50	5-10
cleaned	5.31	18.54	2.50	10-20

DEPTH ANALYSIS (µg/g):LOCHARBRIGGS /AFTER SO_2 EXPOSURE

stone	chloride	nitrate	sulphate	Depth/mm
control	6.83	18.16	9.27	0-2
control	2.96	22.50	7.26	2-5
control	4.33	16.45	0.00	5-10
control	2.86	16.96	0.00	10-20
cleaned	8.67	32.75	12.88	0-2
cleaned	7.76	34.40	7.91	2-5
cleaned	4.69	26.22	10.78	5-10
cleaned	5.13	29.12	8.73	10-20

%CHANGES WITH EXPOSURE

stone	chloride	nitrate	sulphate	Depth/mm
control	133.72	1.38	85.44	0-2
control	17.72	43.59	81.52	2-5
control	-77.31	-42.53	-100.00	5-10
control	-62.49	-9.79	-100.00	10-20
cleaned	14.05	-2.44	415.13	0-2
cleaned	165.35	42.42	216.48	2-5
cleaned	-24.91	-25.82	331.00	5-10
cleaned	-3.42	57.08	249.07	10-20

Appendix 7.2 Depth analysis of soluble anions in Crossland Hill control and cleaned sandstone

DEPTH ANALYSIS (μg/g):CROSSLAND /BEFORE EXPOSURE				
Stone	Chloride	Nitrate	Sulphate	Depth/mm
Control	25.99	17.34	8.44	0-2
Control	31.14	14.91	10.49	2-5
Control	45.63	25.73	12.89	5-10
Cleaned	46.82	29.90	13.10	0-2
Cleaned	41.19	20.89	10.79	2-5
Cleaned	42.83	21.35	9.76	5-10
DEPTH ANALYSIS (μg/g):CROSSLAND /AFTER SO_2 EXPOSURE				
Stone	chloride	nitrate	sulphate	Depth/mm
Control	32.50	18.66	24.64	0-2
Control	40.03	21.44	23.78	2-5
Control	59.43	27.28	26.22	5-10
Cleaned	41.42	22.06	44.89	0-2
Cleaned	39.12	20.28	34.13	2-5
Cleaned	29.25	21.72	19.95	5-10
%CHANGES WITH EXPOSURE				
Stone	chloride	nitrate	sulphate	Depth/mm
Control	25.04	7.60	192.12	0-2
Control	28.55	43.78	126.80	2-5
Control	30.24	6.03	103.33	5-10
Cleaned	-11.53	-26.23	242.71	0-2
Cleaned	-5.02	-2.93	216.32	2-5
Cleaned	-31.69	1.74	104.40	5-10

Appendix 7.3 Depth analysis of other soluble ions in Locharbriggs sandstone

DEPTH ANALYSIS ((µg/g):LOCHARBRIGGS /BEFORE EXPOSURE				
stone	fluoride	*Sodium*	*Potassium*	Depth/mm
control	0.3	1.51	21.75	0-2
control	0.22	1.32	20.38	2-5
control	0.3	3.07	30.18	5-10
control	0.25	2.57	26.88	10-20
cleaned	26	2.32	33.45	0-2
cleaned	0.23	0.77	26.23	2-5
cleaned	0.24	1.00	20.00	5-10
cleaned	0.17	1.56	21.72	10-20
DEPTH ANALYSIS ((µg/g):LOCHARBRIGGS /AFTER SO_2 EXPOSURE				
stone	fluoride	Sodium	Potassium	Depth/mm
control	0.15	1.05	22.44	0-2
control	0.19	1.60	29.26	2-5
control	0.14	2.68	22.81	5-10
control	0.14	1.21	24.24	10-20
cleaned	0.30	2.35	32.15	0-2
cleaned	0.28	1.98	32.61	2-5
cleaned	0.22	1.52	31.29	5-10
cleaned	0.22	2.45	34.12	10-20
%CHANGES WITH EXPOSURE				
stone	fluoride	Sodium	Potassium	Depth/mm
control	-49.30	-30.25	3.17	0-2
control	-14.32	21.19	43.59	2-5
control	-54.05	-12.68	-24.41	5-10
control	-43.16	-53.12	-9.79	10-20
cleaned	-98.83	1.49	-3.89	0-2
cleaned	20.63	158.65	24.33	2-5
cleaned	-7.11	51.99	56.44	5-10
cleaned	31.79	57.08	57.08	10-20

Appendix 7.4a Leaching trends for soluble ions for Locharbriggs sandstone

LEACHING ANALYSIS (µg/g):LOCHARBRIGGS /BEFORE EXPOSURE						
Day	*Sodium*	*Potassium*	*Magnesium*	*Chloride*	*Nitrate*	*Sulphate*
3	2.70	0.57	0.25	1.66	<0.1	0.47
10	5.70	1.41	0.50	3.01	<0.1	0.97
20	9.00	2.39	0.80	4.55	<0.1	1.74
LEACHING ANALYSIS (µg/g):LOCHARBRIGGS /AFTER EXPOSURE						
Day	*Sodium*	*Potassium*	*Magnesium*	*Chloride*	*Nitrate*	*Sulphate*
3	1.40	0.06	0.07	1.64	<0.1	22.62
10	2.90	0.22	0.15	3.73	0.18	49.38
20	4.60	0.42	0.23	6.00	0.18	79.64

Appendix 7.4b Leaching trends for soluble ions for Crossland Hill sandstone

LEACHING ANALYSIS (µg/g):CROSSLAND HILL /BEFORE EXPOSURE						
Day	*Sodium*	*Potassium*	*Magnesium*	*Chloride*	*Nitrate*	*Sulphate*
3	1.20	0.11	1.12	0.80	0.00	0.00
10	3.00	0.25	2.69	1.69	0.00	0.18
20	5.10	0.47	4.69	2.48	0.00	0.18

LEACHING ANALYSIS (µg/g):LOCHARBRIGGS /AFTER EXPOSURE						
Day	*Sodium*	*Potassium*	*Magnesium*	*Chloride*	*Nitrate*	*Sulphate*
3	1.00	0.01	0.05	1.65	0.00	26.85
10	2.50	0.01	0.10	2.44	0.00	63.45
20	4.50	0.04	0.18	3.45	0.00	105.35

Appendix 8.1 Chemical analysis for soluble ions after exposure at depth zones of 0-2, 2-5, 5-10 and 10-20 mm for the Locharbriggs and 0-2, 2-5 and 5-10 mm for Crossland Hill.

DEPTH ANALYSIS (mol/kg):LOCHARBRIGGS CONTROL/FIELD								
stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	depth/mm
Glasgow	87.73	22.85	28.39	35.91	53.88	44.37	10.2	0-2
Glasgow	87.53	15.21	29.39	36.31	64.66	63.39	10.2	2-5
Glasgow	130.73	17.2	28.79	44.68	53.88	44.37	10.2	5-10
Glasgow	88.13	7.56	26.79	36.31	48.49	47.54	10.2	10-20
Aberdeen	95.16	19.64	35.6	36.85	75.44	63.39	10.2	0-2
Aberdeen	95.77	16.87	37.4	102.81	64.66	57.05	10.2	2-5
Aberdeen	143.59	24.63	45.41	95.47	97	95.09	10.2	5-10
Aberdeen	96.57	20.86	38.81	2.72	70.05	60.22	10.2	10-20
Banff	119.48	13.43	26.59	3.75	37.72	9.5	10.2	0-2
Banff	128.32	28.51	30.19	2.41	70.05	12.67	10.2	2-5
Banff	81.1	7.56	18.38	2.9	64.66	12.67	10.2	5-10
Banff	102.4	7.56	27.39	3.05	26.94	6.33	10.2	10-20
Dunkeld	93.96	13.07	34	4.6	64.66	57.05	10.2	0-2
Dunkeld	144.79	27.49	37.2	4.74	80.82	63.39	10.2	2-5
Dunkeld	103.4	5.86	27.19	4.08	75.44	79.24	10.2	5-10
Dunkeld	85.12	5.86	18.38	0.62	86.21	69.73	10.2	10-20
DEPTH ANALYSIS (mol/kg):LOCHARBRIGGS CLEANED/FIELD								
stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	depth/mm
Glasgow	90.49	7.14	25.6	33.72	53.88	31.69	10.2	0-2
Glasgow	77	15.93	27.41	31.78	64.66	38.03	10.2	2-5
Glasgow	94.51	21.31	29.82	35.91	64.66	41.2	10.2	5-10
Glasgow	83.86	7.14	16.96	37.26	43.1	38.03	10.2	10-20
Aberdeen	101.34	18.35	47.1	21.94	64.66	31.69	10.2	0-2
Aberdeen	93.31	21.97	42.28	23.71	70.05	44.37	10.2	2-5
Aberdeen	101.95	7.14	26.81	29.51	53.88	50.71	10.2	5-10
Aberdeen	84.67	7.14	16.96	32.85	43.1	63.39	10.2	10-20
Banff	102.95	16.04	26.6	2.35	64.66	28.52	10.2	0-2
Banff	87.48	7.14	16.96	2.67	16.16	12.67	10.2	2-5
Banff	95.92	7.14	16.96	3.05	26.94	19.01	10.2	5-10
Banff	102.55	17.14	27.01	3.92	64.66	69.73	10.2	10-20
Dunkeld	82.25	7.14	16.04	3.07	53.88	22.18	10.2	0-2
Dunkeld	87.68	14.83	7.14	2.87	53.88	12.67	10.2	2-5
Dunkeld	96.72	16.7	7.14	3.15	64.66	19.01	10.2	5-10
Dunkeld	102.95	14.39	17.14	3.89	64.66	38.03	10.2	10-20

DEPTH ANALYSIS (mol/kg):CROSSLAND CONTROL/FIELD

stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	depth
Glasgow	63.13	8.5	20.65	2.91	67.63	46.41	16	0-2
Glasgow	132.89	24.68	35.28	2.84	78.91	53.05	10.67	2-5
Glasgow	124.08	20.08	33.7	2.32	101.45	66.31	21.34	5-10
Aberdeen	63.13	8.5	20.65	3.16	46.93	30.37	17.77	0-2
Aberdeen	120.7	19.7	31.9	3.17	56.32	49.7	17.77	2-5
Aberdeen	99.48	8.5	32.13	3.64	46.93	33.13	8.88	5-10
Banff	110.54	23.31	41.77	3.78	60.54	42.73	22.92	0-2
Banff	149.37	39.31	51.97	2.83	84.76	49.86	11.46	2-5
Banff	151.18	35.9	44.87	3.51	108.98	56.98	22.92	5-10
Dunkeld	120.7	30.81	42.55	4.2	76.06	52.2	24	0-2
Dunkeld	99.48	23.31	42.68	4.19	76.06	44.74	24	2-5
Dunkeld	112.34	32.73	42.93	3.84	88.75	44.74	24	5-10

DEPTH ANALYSIS (mol/kg):CROSSLAND CLEANED/FIELD

stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	depth
Glasgow	54.07	6.37	15.14	2.79	67.63	46.41	16	0-2
Glasgow	106.09	17.36	27.7	2.43	62	53.05	10.67	2-5
Glasgow	92.28	14.32	24.11	2.36	67.63	66.31	21.34	5-10
Aberdeen	54.07	6.37	15.14	4.17	61.02	38.65	17.77	0-2
Aberdeen	89.23	15.3	24.29	2.6	56.32	38.65	17.77	2-5
Aberdeen	97.66	18.93	25.19	2.14	56.32	38.65	8.88	5-10
Banff	75.95	19.96	30.91	2.73	72.65	42.73	22.92	0-2
Banff	84.92	26.85	36.04	2.89	60.54	42.73	11.46	2-5
Banff	78.46	24.4	34.91	3.03	84.76	42.73	22.92	5-10
Dunkeld	89.23	26	36.14	3.26	88.75	67.12	24	0-2
Dunkeld	97.66	28.44	36.66	3.45	101.43	74.58	24	2-5
Dunkeld	90.48	27.18	35.94	3.8	101.43	59.66	24	5-10

Appendix 8.2 Chemical analysis for soluble ions after exposure at 0, 5, 15 and 30 days for the Locharbriggs and the Crossland Hill sandstones.

LEACHING (mg/L):LOCHARBRIGGS/FIELD								
stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	time
Glasgow	1.29	1.32	0.44	0.01	0.5	0.6	0.1	0
Glasgow	18.58	4.67	1.41	0.03	5.3	1.6	0.2	5
Glasgow	28.45	6.82	2.13	0.1	15.3	2.9	0.5	15
Glasgow	38.23	6.55	2.99	0.24	25.3	4.5	0.8	30
Aberdeen	3.59	2.37	0.81	0.07	1.7	0.6	0.4	0
Aberdeen	10.8	6.04	2.18	0.14	4.9	1.9	1.3	5
Aberdeen	20.6	10.95	4.61	0.29	11.9	3.7	3.3	15
Aberdeen	30.51	16.81	8.54	0.44	18.9	5.8	5.2	30
Banff	1.37	0.67	0.44	0.01	0.3	0	0	0
Banff	6.86	1.45	0.86	0.04	3.2	0.6	0.3	5
Banff	8.55	1.59	1.31	0.16	13.2	1.5	0.7	15
Banff	6.71	1.43	0.93	0.18	23.2	2.6	1.2	30
Dunkeld	1.31	0.29	0.46	0.06	0.9	0.4	0	0
Dunkeld	3.34	1.26	1.27	0.07	2.3	0.75	0.1	5
Dunkeld	5.87	2.65	2.21	0.13	5.3	1.25	0.1	15
Dunkeld	8.54	4.26	3.07	0.2	7.3	1.75	0.1	30
LEACHING (mg/L):CROSSLAND/FIELD								
stone	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	time
Glasgow	1.72	0.71	0.44	0.02	0.4	0	0.1	0
Glasgow	14.08	4.03	1.54	0.03	3.7	0	0.5	5
Glasgow	29.4	6.45	2.8	0.09	8.5	0.1	10.5	15
Glasgow	37.24	8.12	3.44	0.12	10.5	0.2	20.5	30
Aberdeen	3.94	2.42	0.93	0.04	1.3	0.3	0.1	0
Aberdeen	17.09	7.43	2.91	0.05	4.2	0.9	0.6	5
Aberdeen	43.79	19.06	6.31	0.13	11.2	2	1.6	15
Aberdeen	73.62	35	10.02	0.22	20.9	3.3	3.6	30
Banff	1.59	0.23	0.44	0.01	0.3	0	0.1	0
Banff	11.56	2.69	1.14	0.02	2.9	0.2	0.4	5
Banff	28.56	4.87	2.37	0.08	8	0.7	10.4	15
Banff	38.2	6.5	2.93	0.11	18	1.3	12.4	30
Dunkeld	1.2	1.07	0.46	0.07	0.8	0.6	0.1	0
Dunkeld	3.54	2.83	1.21	0.05	1.9	1.2	0.2	5
Dunkeld	7.49	5.68	2.24	0.07	3.9	1.7	0.4	15
Dunkeld	12.03	9.37	3.22	0.1	6.2	2.2	0.6	30

Appendix 8.3 Data matrix for the principal components analysis

LOCHARBRIGGS/CONTROL									
location	chloride	sulphate	nitrate	fluoride	sodium	potassium	rainfall	temperature	gale
1	-37.26	-61.99	-20.32	-44.95	-83.32	-35.49	930.5	11.1	6
1	-81	-97.21	13.83	-44.34	-69.98	-1.48	930.5	11.1	6
1	12.26	-58.55	11.5	-31.5	-74.98	-53.49	930.5	11.1	6
1	-41.1	-94.88	-12.28	-44.34	-69.98	-44.03	930.5	11.1	6
2	-31.95	-67.33	-0.08	-43.51	-76.65	-7.84	895.5	8.7	4
2	-79.21	-96.91	44.85	57.61	-69.98	-11.33	895.5	8.7	4
2	23.31	-40.65	75.87	46.36	-54.95	-0.32	895.5	8.7	4
2	-35.46	-85.86	27.08	-95.83	-56.64	-29.1	895.5	8.7	4
3	-14.56	-77.66	-25.37	-94.25	-88.32	-86.19	367	6.9	2.5
3	-72.15	-94.78	16.92	-96.31	-67.48	-80.31	367	6.9	2.5
3	-30.36	-81.78	-28.81	-95.55	-69.97	-86.72	367	6.9	2.5
3	-31.56	-94.88	-10.31	-95.32	-83.32	-92.55	367	6.9	2.5
4	-32.81	-78.26	-4.57	-92.95	-79.98	-17.05	434	6.5	0.5
4	-68.57	-94.96	44.07	-92.73	-62.48	-1.48	434	6.5	0.5
4	-11.21	-85.88	5.31	-93.75	-64.96	-16.94	434	6.5	0.5
4	-43.11	-96.03	-39.82	-99.05	-46.64	-17.91	434	6.5	0.5
LOCHARBRIGGS/CLEANED									
location	chloride	sulphate	nitrate	fluoride	sodium	potassium	rainfall	temperature	gale
1	-20.24	-82.14	-18.34	-98.62	-97.5	-70.07	930.5	11.1	6
1	-28.74	-60.15	-40.59	-97.33	-96.57	-54.26	930.5	11.1	6
1	13.63	-46.69	15.49	-96.33	-94	-46.28	930.5	11.1	6
1	6.1	-82.14	-34.31	-88.78	-92	-44.71	930.5	11.1	6
2	-10.67	-54.09	50.24	-99.1	-97	-70.07	895.5	8.7	4
2	-13.65	-45.03	-8.37	-98.01	-96.28	-46.63	895.5	8.7	4
2	22.58	-82.14	3.83	-96.98	-95	-33.89	895.5	8.7	4
2	7.12	-82.14	-34.31	-90.11	-92	-7.84	895.5	8.7	4
3	-9.26	-59.87	-15.15	-99.9	-97	-73.06	367	6.9	2.5
3	-19.04	-82.14	-63.24	-99.78	-99.14	-84.76	367	6.9	2.5
3	15.33	-82.14	-34.31	-99.69	-97.5	-75.22	367	6.9	2.5
3	29.74	-57.12	4.61	-98.82	-87.99	1.38	367	6.9	2.5
4	-27.5	-82.14	-48.84	-99.87	-97.5	-79.05	434	6.5	0.5
4	-18.86	-62.9	-84.53	-99.76	-97.14	-84.76	434	6.5	0.5
4	16.29	-58.22	-72.35	-99.68	-94	-75.22	434	6.5	0.5
4	30.25	-64	-33.62	-98.83	-87.99	-44.71	434	6.5	0.5

CROSSLAND HILL/CONTROL										
location	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	rainfall	T/°C	gale
1	-57.54	-91	-99.22	-95.54	-82.04	-32.52	56.86	930.5	11.1	6
1	-74.28	-56.7	-96.93	-95.65	-88.73	-17.55	4.61	930.5	11.1	6
1	-66.56	-56.64	-92.57	-96.44	-90.58	-30.5	109.22	930.5	11.1	6
2	-57.54	-91	-99.22	-95.16	-87.54	-55.84	74.22	895.5	8.7	4
2	-76.64	-65.44	-97.23	-95.14	-91.95	-22.75	74.22	895.5	8.7	4
2	-73.19	-81.65	92.92	-94.42	-95.64	-65.28	-12.94	895.5	8.7	4
3	-25.66	-75.33	-98.42	-94.21	-83.92	-37.87	124.71	367	6.9	2.5
3	-71.09	-31.04	-95.48	-95.66	-87.89	-22.51	12.35	367	6.9	2.5
3	-59.26	-22.48	-90.11	-94.62	-89.88	-40.28	124.71	367	6.9	2.5
4	-18.82	-67.39	-98.39	-93.56	-79.8	-24.11	135.29	434	6.5	0.5
4	-80.75	-59.11	-96.29	-93.58	-89.13	-30.46	135.29	434	6.5	0.5
4	-69.72	-29.32	-90.54	-94.11	-91.76	-53.11	135.29	434	6.5	0.5
CROSSLAND HILL/CLEANED										
location	chloride	sulphate	nitrate	fluoride	sodium	potassium	magnesium	rainfall	T/°C	gale
1	-70.98	-91.71	-85.46	-99.8	-96.41	-56.16	56.86	930.5	11.1	6
1	-54.61	-71.27	-45.18	-99.78	-94.24	-36.19	4.61	930.5	11.1	6
1	-40.08	-73.56	-21.13	-99.73	-91.62	-13.55	109.22	930.5	11.1	6
2	-70.98	-91.71	-85.46	-99.71	-96.76	-63.49	74.22	895.5	8.7	4
2	-61.83	-74.68	-51.93	-99.77	-94.77	-53.51	74.22	895.5	8.7	4
2	-36.58	-65.05	-17.6	-99.75	-93.02	-49.61	-12.94	895.5	8.7	4
3	-59.23	-74.04	-70.32	-99.81	-96.14	-59.64	124.71	367	6.9	2.5
3	-63.67	-55.56	-28.68	-99.74	-94.38	-48.6	12.35	367	6.9	2.5
3	-49.05	-54.96	14.2	-99.65	-89.49	-44.29	124.71	367	6.9	2.5
4	-52.1	-66.18	-65.3	-99.77	-95.29	-36.6	135.29	434	6.5	0.5
4	-58.22	-52.93	-27.45	-99.69	-90.58	-10.3	135.29	434	6.5	0.5
4	-41.25	-49.82	17.57	-99.56	-87.43	-22.22	135.29	434	6.5	0.5

Appendix 8.4 Summary of the degrees of freedom and critical F values for the two sandstones.

Source of variation	*Degrees of freedom*		
	Locharbriggs	**Crossland Hill**	
	DEPTH/LOCATION	DEPTH	LOCATION
Between sample	h – 1 = 3	h – 1 = 2	3
Within sample	h(n – 1) = 12	h(n – 1) = 9	8
Critical value[1], F P = 0.05	$F_{3,12} = 3.49$	$F_{3,8} = 4.06$	$F_{2,9} = 4.25$

h and n represent the different depths and locations. If Fvalues > Ftabulated then the sample means differ significantly and the null hypothesis is rejected.

[1] Miller and Miller (1993).

Appendix 8.5 Example of one-way ANOVA and correlation analysis for Locharbriggs sandstone

LOCHARBRIGGS CONTROL

```
                            - - - - -  O N E W A Y  - - - - -


      Variable  CHLORIDE
   By Variable  DEPTH

                                    Analysis of Variance


                                    Sum of        Mean                F        F
        Source             D.F.    Squares       Squares            Ratio    Prob.

Between Groups               3   11118.6893    3706.2298          20.0481    .0001
Within Groups               12    2218.4075     184.8673
Total                       15   13337.0968



                                   Standard   Standard
Group        Count       Mean     Deviation     Error     95 Pct Conf Int for Mean

Grp 1            4   -29.1450      9.9979      4.9990    -45.0537   TO    -13.2363
Grp 2            4   -75.2325      5.8588      2.9294    -84.5550   TO    -65.9100
Grp 3            4    -1.5000     24.0282     12.0141    -39.7336   TO     36.7336
Grp 4            4   -37.8075      5.2757      2.6379    -46.2022   TO    -29.4128

Total           16   -35.9213     29.8184      7.4546    -51.8104   TO    -20.0321


GROUP          MINIMUM      MAXIMUM

Grp 1         -37.2600     -14.5600
Grp 2         -81.0000     -68.5700
Grp 3         -30.3600      23.3100
Grp 4         -43.1100     -31.5600

TOTAL         -81.0000      23.3100
```

```
                    - - - - -  O N E W A Y  - - - - -

        Variable  CHLORIDE
     By Variable  LOCATION   location

                              Analysis of Variance

                                   Sum of         Mean          F      F
       Source             D.F.    Squares        Squares      Ratio  Prob.

Between Groups              3      148.9040       49.6347     .0452  .9866
Within Groups              12    13188.1927     1099.0161
Total                      15    13337.0968


                                       Standard   Standard
Group          Count        Mean     Deviation      Error    95 Pct Conf Int for Mean

Grp 1             4     -36.7750      38.2066     19.1033    -97.5693  TO     24.0193
Grp 2             4     -30.8275      42.0097     21.0049    -97.6734  TO     36.0184
Grp 3             4     -37.1575      24.5809     12.2904    -76.2706  TO      1.9556
Grp 4             4     -38.9250      23.8177     11.9089    -76.8238  TO     -1.0262

Total            16     -35.9213      29.8184      7.4546    -51.8104  TO    -20.0321


GROUP          MINIMUM      MAXIMUM

Grp 1         -81.0000      12.2600
Grp 2         -79.2100      23.3100
Grp 3         -72.1500     -14.5600
Grp 4         -68.5700     -11.2100

TOTAL         -81.0000      23.3100
```

```
                       - -  Correlation Coefficients  - -

              CHLORIDE   FLUORIDE   NITRATE    POTASIUM   SODIUM     SULPHATE

CHLORIDE       1.0000      .1096      .0138     -.1284     -.0424      .7899
              (   16)    (   16)    (   16)    (   16)    (   16)    (   16)
              P= .       P= .686    P= .960    P= .636    P= .876    P= .000

FLUORIDE        .1096     1.0000      .6079      .4299      .0799      .4165
              (   16)    (   16)    (   16)    (   16)    (   16)    (   16)
              P= .686    P= .       P= .012    P= .097    P= .769    P= .109

NITRATE         .0138      .6079     1.0000      .5038      .3528      .2439
              (   16)    (   16)    (   16)    (   16)    (   16)    (   16)
              P= .960    P= .012    P= .       P= .047    P= .180    P= .363

POTASIUM       -.1284      .4299      .5038     1.0000      .4735      .1226
              (   16)    (   16)    (   16)    (   16)    (   16)    (   16)
              P= .636    P= .097    P= .047    P= .       P= .064    P= .651

SODIUM         -.0424      .0799      .3528      .4735     1.0000     -.1173
              (   16)    (   16)    (   16)    (   16)    (   16)    (   16)
              P= .876    P= .769    P= .180    P= .064    P= .       P= .665

SULPHATE        .7899      .4165      .2439      .1226     -.1173     1.0000
              (   16)    (   16)    (   16)    (   16)    (   16)    (   16)
              P= .000    P= .109    P= .363    P= .651    P= .665    P= .

(Coefficient / (Cases) / 2-tailed Significance)

" . " is printed if a coefficient cannot be computed


- - -  P A R T I A L   C O R R E L A T I O N   C O E F F I C I E N T S  - - -

Controlling for..    FLUORIDE  NITRATE   POTASIUM  SULPHATE

              CHLORIDE    SODIUM

CHLORIDE       1.0000      .3375
              (    0)    (   10)
              P= .       P= .283

SODIUM          .3375     1.0000
              (   10)    (    0)
              P= .283    P= .

(Coefficient / (D.F.) / 2-tailed Significance)
```

Appendix 8.6 Multivariate statistical analysis results

LOCHARBRIGGS CONTROL

```
Initial Statistics:


Variable        Communality  *  Factor   Eigenvalue    Pct of Var    Cum Pct
                             *
CHLORIDE            1.00000  *     1       3.79921         42.2         42.2
FLUORIDE            1.00000  *     2       1.98233         22.0         64.2
GALE                1.00000  *     3       1.63123         18.1         82.4
NITRATE             1.00000  *     4        .68663          7.6         90.0
POTASIUM            1.00000  *     5        .47545          5.3         95.3
RAINFALL            1.00000  *     6        .25493          2.8         98.1
SODIUM              1.00000  *     7        .11958          1.3         99.4
SULPHATE            1.00000  *     8        .04345           .5         99.9
TEMPERAT            1.00000  *     9        .00718           .1        100.0

PC     extracted   2 factors.


Rotated Factor Matrix:


                Factor  1     Factor  2

CHLORIDE          .34041       -.22469
FLUORIDE          .66841        .52480
GALE              .91751       -.03669
NITRATE           .21084        .76405
POTASIUM          .11924        .84280
RAINFALL          .86627        .39383
SODIUM           -.28365        .72216
SULPHATE          .61452       -.01704
TEMPERAT          .89800        .07239
```

```
                         Canonical Discriminant Functions


                 Pct of    Cum   Canonical  After  Wilks'
Fcn Eigenvalue Variance    Pct      Corr      Fcn  Lambda   Chi-square   df   Sig

                                           :    0 .031721     34.508     18  .0109
 1*    10.1184    86.88   86.88     .9540  :    1 .352685     10.422     10  .4043
 2*     1.2889    11.07   97.95     .7504  :    2 .807278      2.141      4  .7099
 3*      .2387     2.05  100.00     .4390  :
```

LOCHARBRIGGS CLEANED

```
Initial Statistics:


Variable      Communality  *  Factor   Eigenvalue   Pct of Var   Cum Pct
                           *
CHLORIDE          1.00000  *     1       3.74158       41.6        41.6
FLUORIDE          1.00000  *     2       2.49464       27.7        69.3
GALE              1.00000  *     3       1.41620       15.7        85.0
NITRATE           1.00000  *     4        .58849        6.5        91.6
POTASIUM          1.00000  *     5        .30178        3.4        94.9
RAINFALL          1.00000  *     6        .20261        2.3        97.2
SODIUM            1.00000  *     7        .12973        1.4        98.6
SULPHATE          1.00000  *     8        .11868        1.3        99.9
TEMPERAT          1.00000  *     9        .00628         .1       100.0



               Factor  1     Factor  2

CHLORIDE        -.13472        .88426
FLUORIDE         .65010        .37012
GALE             .96144       -.06258
NITRATE          .51909        .29328
POTASIUM         .36885        .84113
RAINFALL         .94842       -.02089
SODIUM          -.00687        .94694
SULPHATE         .01973        .16404
TEMPERAT         .95731       -.09386
```

```
Canonical Discriminant Functions


               Pct of   Cum  Canonical  After  Wilks'
Fcn Eigenvalue Variance Pct     Corr      Fcn  Lambda  Chi-square  df   Sig

                                       :   0 .051533    29.655     18  .0409
1*   10.2507   93.51   93.51    .9545 :   1 .579780     5.451     10  .8591
2*     .6936    6.33   99.83    .6400 :   2 .981924      .182      4  .9961
3*     .0184     .17  100.00    .1344 :
```

CROSSLAND HILL CONTROL

```
Initial Statistics:


Variable      Communality  *  Factor   Eigenvalue   Pct of Var   Cum Pct
                           *
CHLORIDE         1.00000   *     1      4.33380        43.3         43.3
FLUORIDE         1.00000   *     2      2.36987        23.7         67.0
GALE             1.00000   *     3      1.71734        17.2         84.2
MAGNESIU         1.00000   *     4       .66170         6.6         90.8
NITRATE          1.00000   *     5       .45770         4.6         95.4
POTASIUM         1.00000   *     6       .23448         2.3         97.7
RAINFALL         1.00000   *     7       .10435         1.0         98.8
SODIUM           1.00000   *     8       .06736          .7         99.5
SULPHATE         1.00000   *     9       .04461          .4         99.9
TEMPERAT         1.00000   *    10       .00879          .1        100.0

PC    extracted   2 factors.

Rotated Factor Matrix:


              Factor  1     Factor  2

CHLORIDE       -.30138        .62940
FLUORIDE       -.84595       -.02852
GALE            .97094       -.05519
MAGNESIU       -.60980        .46630
NITRATE         .03642       -.82700
POTASIUM        .22348        .67476
RAINFALL        .88821       -.24875
SODIUM         -.05967        .88474
SULPHATE       -.44775       -.05739


                  Canonical Discriminant Functions


              Pct of    Cum   Canonical  After  Wilks'
Fcn Eigenvalue Variance  Pct     Corr       Fcn  Lambda   Chi-square  df   Sig

                                         :   0 .013578     23.646    21  .3105
 1*   12.8238    81.74   81.74    .9632 :   1 .187696      9.201    12  .6857
 2*    2.2006    14.03   95.76    .8292 :   2 .600738      2.803     5  .7304
 3*     .6646     4.24  100.00    .6319 :
```

CROSSLAND HILL CLEANED

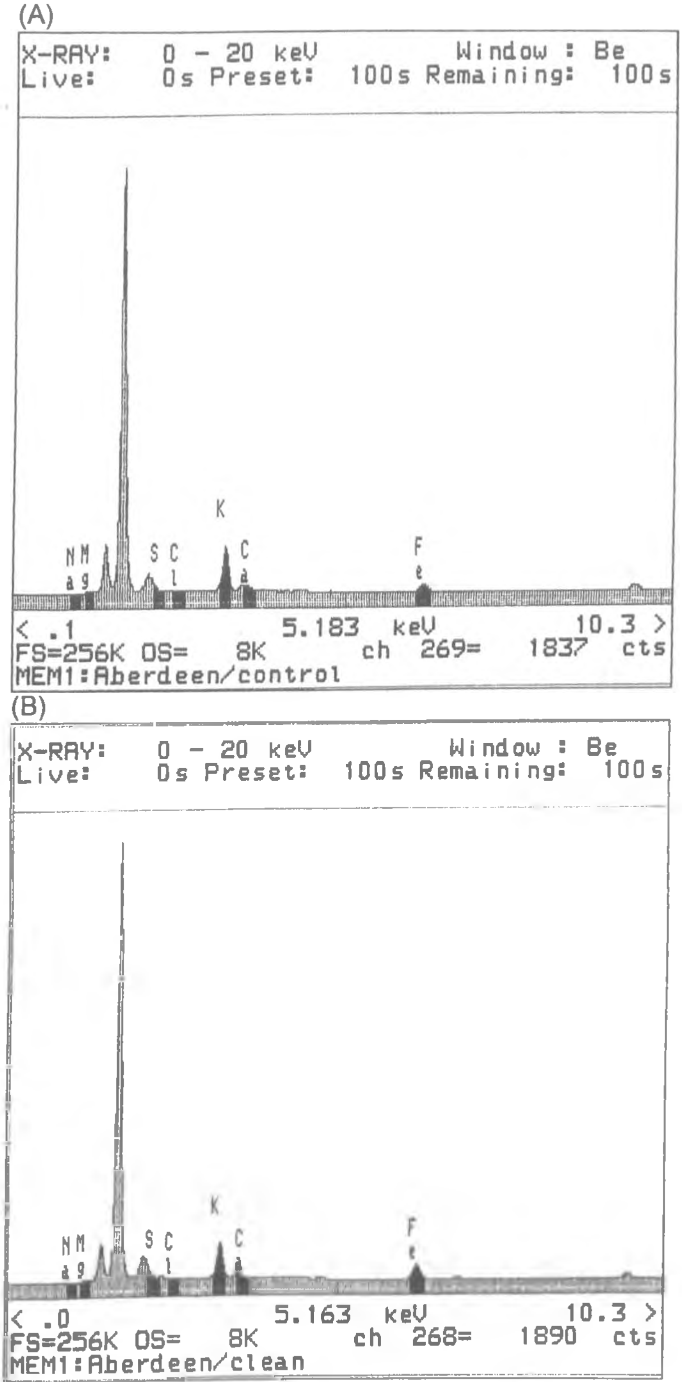
```
Initial Statistics:


Variable      Communality  *  Factor   Eigenvalue   Pct of Var   Cum Pct
                           *
CHLORIDE         1.00000   *     1       6.23805        56.7        56.7
FLUORIDE         1.00000   *     2       2.54266        23.1        79.8
GALE             1.00000   *     3        .91779         8.3        88.2
MAGNESIU         1.00000   *     4        .57778         5.3        93.4
NITRATE          1.00000   *     5        .38267         3.5        96.9
POTASIUM         1.00000   *     6        .25779         2.3        99.2
RAINFALL         1.00000   *     7        .05627          .5        99.8
SEAEXP           1.00000   *     8        .01815          .2        99.9
SODIUM           1.00000   *     9        .00709          .1       100.0
SULPHATE         1.00000   *    10        .00176          .0       100.0
TEMPERAT         1.00000   *    11        .00000          .0       100.0


Rotated Factor Matrix:


             Factor  1     Factor  2

CHLORIDE        .06267        .82919
FLUORIDE      -.38399         .72437
GALE            .95685       -.19222
MAGNESIU      -.61796         .16833
NITRATE       -.19134         .92905
POTASIUM      -.10222         .76241
RAINFALL        .91808       -.14381
SEAEXP          .96548       -.19322
```

```
                       Canonical Discriminant Functions


                Pct of    Cum  Canonical  After  Wilks'
Fcn Eigenvalue Variance   Pct     Corr      Fcn  Lambda  Chi-square  df   Sig

                                          :   0 .000980     38.103   21  .0125
 1*    81.0948    91.77  91.77     .9939 :   1 .080471     13.859   12  .3098
 2*     6.6451     7.52  99.29     .9323 :   2 .615211      2.672    5  .7504
 3*      .6255      .71 100.00     .6203 :
```

Appendix 8.7 **Initial and final values for the colour components brightness (L), green to red (a) and blue to yellow (b).**

L	LOCHARBRIGGS CONTROL			LOCHARBRIGGS CLEANED		
Site	Before	After	increment	Before	After	increment
Glasgow	56.65	36.27	-20.38	58.7	43.51	-15.19
Aberdeen	56.65	50.5	-6.15	58.67	43.46	-15.21
Banff	63.36	46.97	-16.39	62.81	47.18	-15.63
Dunkeld	60.53	37.82	-22.71	62.92	46.57	-16.35
L	**CROSSLAND CONTROL**			**CROSSLAND CLEANED**		
Site	Before	After	increment	Before	After	increment
Glasgow	60.76	49.3	-11.46	63.49	54.05	-9.44
Aberdeen	60.76	59.22	-1.54	63.49	58.02	-5.47
Banff	69.26	58.82	-10.44	69.26	59.53	-9.73
Dunkeld	68.73	58.85	-9.88	66.93	55.24	-11.69
a	**LOCHARBRIGGS CONTROL**			**LOCHARBRIGGS CLEANED**		
Site	Before	After	increment	Before	After	increment
Glasgow	3.6	7.85	4.25	4.38	9.25	4.87
Aberdeen	3.6	8.7	5.1	4.5	10.56	6.06
Banff	6.8	14.4	7.6	5.47	11.77	6.3
Dunkeld	5.06	6.92	1.86	6.25	9.86	3.61
a	**CROSSLAND CONTROL**			**CROSSLAND CLEANED**		
Site	Before	After	Increment	Before	After	Increment
Glasgow	0.43	-0.37	-0.8	1.22	0.6	-0.62
Aberdeen	0.43	2.02	1.59	0.9	0.37	-0.53
Banff	1.43	1.37	-0.06	0.78	-0.4	-1.18
Dunkeld	0.26	-1.1	-1.36	0.93	-0.82	-1.75
b	**LOCHARBRIGGS CONTROL**			**LOCHARBRIGGS CLEANED**		
Site	Before	After	Increment	Before	After	Increment
Glasgow	9.45	12.75	3.3	10.97	15.49	4.52
Aberdeen	9.45	15.85	6.4	10.95	16.19	5.24
Banff	11.83	18.62	6.79	11.41	16.68	5.27
Dunkeld	10.76	13.7	2.94	12.05	17.01	4.96
b	**CROSSLAND CONTROL**			**CROSSLAND CLEANED**		
Site	Before	After	Increment	Before	After	Increment
Glasgow	11.16	16.2	5.04	12.6	17.26	4.66
Aberdeen	11.16	19.77	8.61	12.6	16.45	3.85
Banff	13.73	18.92	5.19	12.13	15.21	3.08
Dunkeld	11.66	15.7	4.04	13.26	19.04	5.78

Appendix 8.8 The EDX analysis for Locharbriggs and Crossland Hill stones



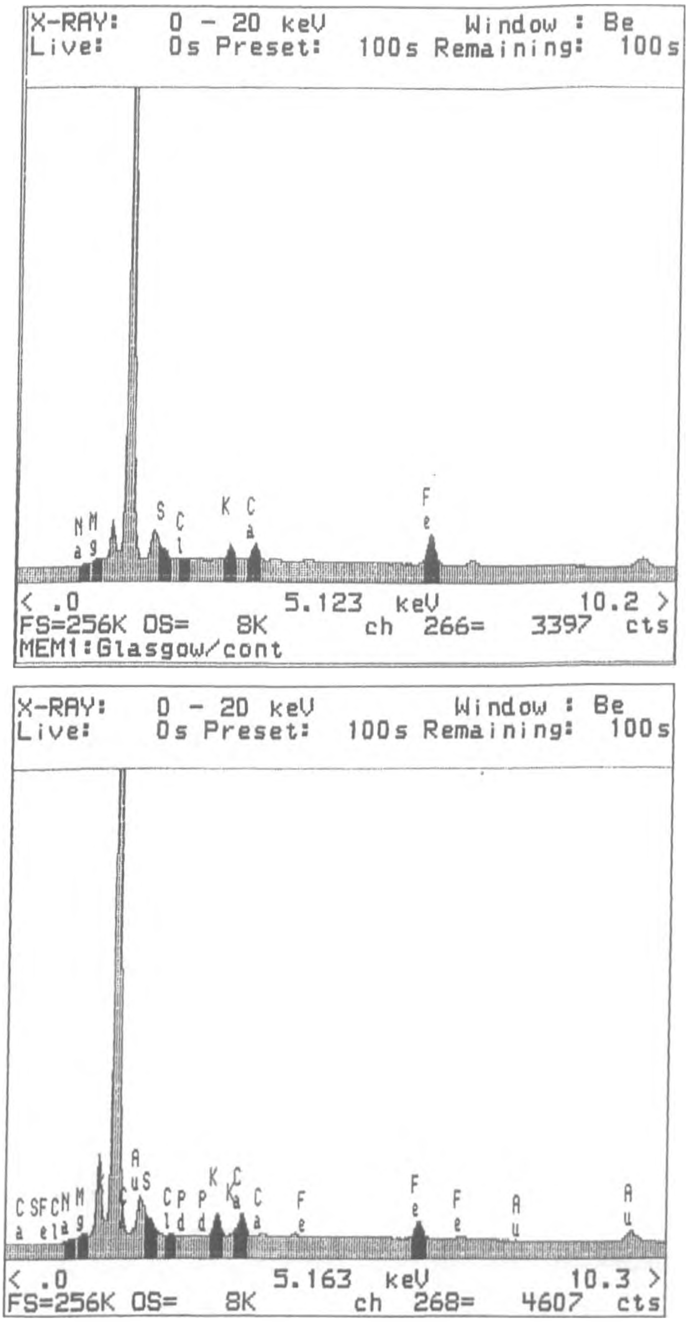
(A)

```
X-RAY:    0 - 20 keV          Window : Be
Live:     0s Preset:   100s Remaining:   100s
< .1              5.183  keV          10.3 >
FS=256K OS=   8K       ch  269=    1837   cts
MEM1:Aberdeen/control
```

(B)

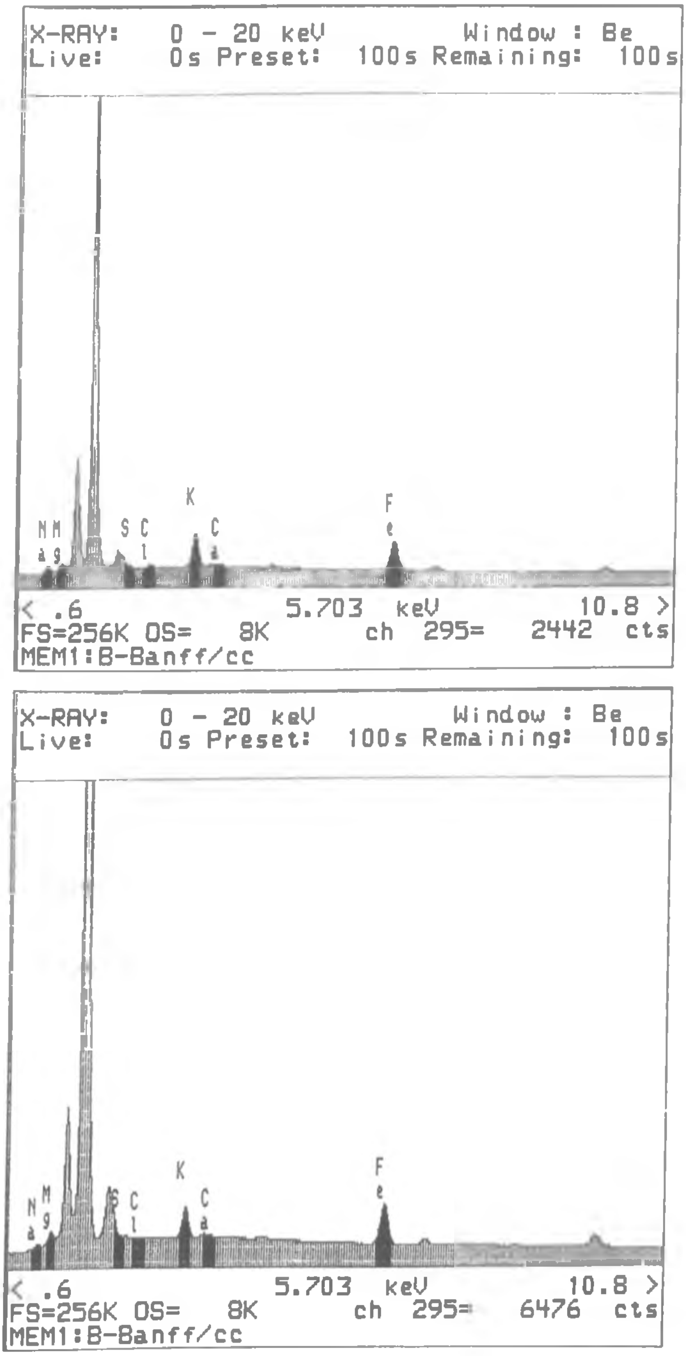
```
X-RAY:    0 - 20 keV          Window : Be
Live:     0s Preset:   100s Remaining:   100s
< .0              5.163  keV          10.3 >
FS=256K OS=   8K       ch  268=    1890   cts
MEM1:Aberdeen/clean
```

EDX analysis of the potassium feldspar shown in Plates 8.2a-b


```
X-RAY:    0 - 20 keV          Window : Be
Live:     0s Preset:   100s Remaining:  100s
< .0              5.123  keV          10.2 >
FS=256K OS=    8K       ch  266=     3397  cts
MEM1:Glasgow/cont
```

```
X-RAY:    0 - 20 keV          Window : Be
Live:     0s Preset:   100s Remaining:  100s
< .0              5.163  keV          10.3 >
FS=256K OS=    8K       ch  268=     4607  cts
```

EDX analysis of the Locharbriggs surface in Plates 8.1a-b respectively



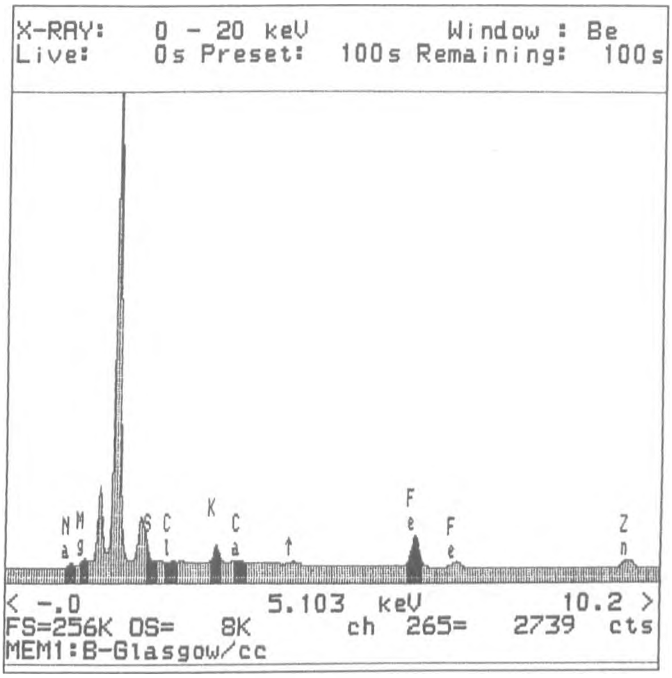
```
X-RAY:    0 - 20 keV          Window : Be
Live:     0s Preset:  100s Remaining:  100s
```

```
< .6              5.703  keV          10.8 >
FS=256K OS=    8K      ch  295=    2442  cts
MEM1:B-Banff/cc
```

```
X-RAY:    0 - 20 keV          Window : Be
Live:     0s Preset:  100s Remaining:  100s
```

```
< .6              5.703  keV          10.8 >
FS=256K OS=    8K      ch  295=    6476  cts
MEM1:B-Banff/cc
```

EDX analysis of the Crossland Hill surface in Plates 8.4a-b respectively



```
X-RAY:    0 - 20 keV          Window : Be
Live:     0s Preset:  100s Remaining:  100s
```

```
< -.0             5.103  keV          10.2 >
FS=256K OS=   8K        ch  265=   2739  cts
MEM1:B-Glasgow/cc
```

EDX analysis of the Crossland Hill surface in Plate 8.3a

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