Consolidation, protection and surface characterisation of marble antiquities

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Consolidation, Protection and Surface Characterisation of Marble Antiquities

By

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BSc. (Hons)

A doctoral thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

September 2000

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To Marcus and my parents for their love and support
ACKNOWLEDGEMENTS

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ABSTRACT

The surface characteristics of the Ince Blundell collection was used to develop a consolidation procedure and weathering protection layer that is sympathetic to the original antiquity. Weathered marble from the collection has been characterised by DRIFT spectroscopy, XPS, SEM and mercury porosimetry. Results have been compared to non-weathered Carrara marble and powdered Italian marble. Highly friable regions, that required consolidation, were mainly comprised of calcite and the porosity of the substrate was approximately 30%.

The consolidation procedure involves two steps. Firstly a charge stabilised colloidal dispersion reintroduces calcite back into the marble fabric and secondly, limewater nucleates and grows calcite in situ directly onto the original marble and deposited calcium carbonate. Optimisation has been achieved for both steps. For the charge stabilised colloidal dispersion, the electrostatic repulsive forces and van der Waals attractive forces between particles and the marble surface have been studied. From experimental determination of the marble surface potential, (zeta potential), and the theoretical determination of the Hamaker constant and diffuse layer thickness, a colloidal solution at pH 10.5 is used. For the limewater application optimisation was achieved using an atmosphere of CO$_2$ at a flow rate of 1.26 l min$^{-1}$ and a temperature less than 40°C. Laboratory trials on a 2nd Century Roman bust successfully consolidated the friable marble, with no detrimental effects observed.

DRIFT spectroscopy and XPS has been used to quantitatively study the effectiveness of monolayer coatings on the inhibition of calcium sulphate dihydrate formation, under accelerated conditions. Non-coated samples reacted to form two species calcium sulphite and calcium sulphate dihydrate and under the conditions studied no evidence has been found to suggest the sulphate species is formed by conversion of the calcium sulphite. It is postulated that the adsorbed water controls the mechanism and the results correlate to this theory. In terms of protection stearate coated marble gave the best results where at an optimum coating thickness of ~1.2 nm it was found to totally inhibit sulphate formation. Sulphite formation was not inhibited although the product concentration was reduced.
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INTRODUCTION

Calcareous stones such as limestone and calcite marble have, since ancient times, been largely used for monumental and sculptural purposes and are often considered to be synonymous with the idea of eternity. Calcareous stone durability however is not absolute and it is long established that of all the stones they are the most susceptible to many forms of weathering. All stone materials decay with time and these mechanisms that bring about such alterations can be broadly categorised into three areas:

- Physical weathering,
- Chemical weathering,
- Biological weathering.

The study of calcareous stone decay is complex since every stone artefact will have undergone its own unique set of weathering conditions dependent on internal properties and external environmental conditions. The deterioration is therefore the result of the combined action of various weathering processes that may act independently or jointly, running consecutively or concurrently. The eventual outcome for weathered stone, independent of the route by which it attains this state, is the same in that the stone will eventually exhibit loss of intergranular cohesion and is said to be "friable". This condition accelerates decay with the eventual loss of sculptural detailing and bulk material, unless the surface and underlying friable stone can be stabilised by the application of a consolidant.

The application of consolidants to the surface of stone has been a practice used for centuries in an attempt to primarily reinforce the existing material and secondly inhibit further weathering. Diverse types of materials have been applied to surfaces ranging from waxes and oils to fluorinated polymers, often
with little consideration to stone/consolidant compatibility and long term effectiveness.

The aim of this project has been to develop a sympathetic consolidation and weathering protection technique that can be applied to the Ince Blundell collection of marble sculptures held under the care of the National Museums and Galleries on Merseyside, NMGM.

During the 19th century Henry Blundell, collected around 400 classical marble and bronze sculptures, which he displayed within the grounds of his country home at Ince, a few miles north of Liverpool. Having been removed from the warmer climate of southern Europe, the marble surfaces have been exposed to a combination of comparably more extreme weather conditions and an atmosphere heavily contaminated with industrial pollutants. A 150 years of "accelerated" decay has resulted in a significant proportion of the collection exhibiting extremely friable areas with very little cohesive strength between the marble crystals.

The conservation section at NMGM has undertaken a large-scale project of restoration and over the last 10 years has developed new techniques in laser cleaning primarily using Nd-YAG lasers and where decay is very severe stone replication by non-contact methods. It was decided at this point to develop a consolidation procedure that would complement these new methods and a number of criteria discussed at the outset of the research have formed the basis for the approach to the overall aim:

1. Ideally the applied consolidant must be sympathetic to the original material.
2. The consolidant is to be used in conjunction with the laser cleaning technique.
3. The applied consolidant would not be based on an organic polymer where issues such as long term stability, reversibility and laser compatibility are still in question.
4. The applied consolidant and weathering protection must not detract from
the original aesthetic, by the action of colour alteration and the formation of
surface layers.

5. The procedure must allow for retreatment at some later date.

This thesis reports the work, which has been carried out over a three year
period and is described in 3 parts with each part separately focusing on two
areas:

- The development of a consolidation procedure
- The protection from future chemical weathering

**Part 1 - Background and Theory**, is split into three chapters where Chapter 1
reviews the literature on calcareous stone and weathering mechanisms
Chapter 2 reviews existing methods in the conservation of stone objects
including cleaning, consolidation and protection procedures. Chapter 3
outlines the theory of the characterisation techniques used to study the
weathered marble and model compounds.

**Part 2 - Experimental**, describes the methodology design and procedure and
again is split into three chapters. Chapter 4, covers the experimental methods
used for the characterisation of Ince Blundell samples and model materials.
Chapter 5, details the experimental methods in the development of the
consolidation procedure and Chapter 6, reports the design of the weathering
exposure rig for testing of monomolecular coatings and the characterisation of
these coatings.

**Part 3 - Results and Discussion**, is sub-divided into four chapters where
Chapters 7, 8 and 9 each present the findings from the experimental sections
outlined in Chapters 4, 5 and 6 respectively Chapter 10 summarises the main
results and details potential field trials and future work.
PART 1. BACKGROUND AND THEORY
Chapter 1 MARBLE WEATHERING

1.1 Sculptural and Monumental Calcareous Stone Definition

Calcareous stone is a general term that applies to all rocks that are composed of greater than 50% calcium carbonate, \((\text{CaCO}_3)\). Within the context of monumental and sculptural stone, the most commonly used calcareous stones are limestone and calcite marble. Although marble is the most favoured choice for statuary, and is the focus of this thesis, consideration is also given to limestone as it is often associated and confused with marble. Limestone is a UK vernacular, monumental and building material where the large calcium carbonate content means many mechanisms of decay run concurrently with that of marble statuary, and weathering research often considers both stones mutually. There is however substantial differences between these stones that has an effect on the rate of weathering and a brief review of geological terms and differences in petrology is given for both marble and limestone.

1.1.1 Marble and Limestone Rock Type

Stone is a general term applied to all rocks that are quarried for a purpose such as construction, where the term rock refers to material composed of one or more minerals and a mineral is defined as;

"A body produced by the processes of inorganic nature, having usually a definite chemical composition and, if formed under favourable conditions a certain characteristic atomic structure which is expressed in its crystalline form and other physical properties."

As such all rocks are classified by three categories which relate to the process of formation:

- **Igneous rocks** – Crystallised from a magma, of similar composition to the final cooled rock, either below the surface crust or at the surface as a result of volcanic activity.


**Sedimentary rocks** – Formed by a combination of processes including production of a sediment, transportation, deposition by water or wind and finally lithification, which converts loose particles into solid rock. The final stage occurs by the process of compaction, where individual grains are pressed together causing the expulsion of water and rearrangement of particles. Finally the rock is consolidated by the precipitation of minerals between the particles.

**Metamorphic rocks** – Formed by the transformation of existing rocks in the solid state by heat, pressure and chemical action. This may lead solely to the deformation of the crystals and grains or it may be accompanied by the re-crystallisation of some or all of the original minerals to give a more ordered and tightly packed atomic structure.

Limestone is grouped under the sedimentary classification, and numerous types exist dependent on the origin of the sediment and the exact conditions during formation. The calcareous sediment normally accumulated from two main sources: biological organisms or direct chemical precipitation. The resultant biological limestones predominantly consist of whole shells of molluscs or the skeletal remains of coral and other marine organisms (e.g. shelly and clastic limestone). In comparison the chemically formed limestones (oolitic limestone) contain spherical grains of calcium carbonate known as oolites. Oolites formed by precipitation, from charged carbonate waters, concentrically around a small nucleus, often part of a shell. Both sediments are contained within a matrix of calcite, the mineral of calcium carbonate, which acts to consolidate the rock. The calcium carbonate content of limestone is rarely greater than 98%, and often incorporated into the matrix are other minerals, clays and carbonaceous matter that result in the coloration of the limestone. Generally the number of sedimentary components that are dispersed in the calcite matrix define the characteristic physical properties such as texture, and porosity.
The term marble has a number of definitions, which in geology alone are defined as:

"1. A metamorphic rock consisting predominantly of fine - to coarse grained re-cry stallised calcite and/or dolomite..."

(Where dolomite refers to the double carbonate of calcium and magnesium with the mineral composition, CaMg(CO₃)₂.)

"2. In commerce, any crystallised carbonate rock, including true marble and certain types of limestone (orthomarble) that will take a high polish and can be used as architectural or ornamental stone."

The first definition is generally regarded as the true meaning of the term marble and in this thesis marble is taken to refer, solely, to the metamorphic-formed calcite rock. Therefore the correct association of marble with limestone emanates from the process of formation where marble originates from limestone which has been re-cry stallised by heat and pressure.

As the calcite minerals re-cry stallise in the solid state the existing fabric of the limestone is lost, and no true marble has any fossiliferous or detrital remains. This process of formation results in an ordered, equidimensional, arrangement of the calcite mineral that within the metamorphic rock classification is regarded as non-foliated due to the lack of preferred orientation of the crystals as opposed to metamorphosed slate. The variations in types of marble are as numerous as limestone. Often referred to as saccharoidal marble the general texture of the bulk cleaved marble resembles a mass of sugar grains, and as weathering processes occur individual grains detach from the bulk and the surface can be termed as "sugary". The re-cry stallisation process produces an ordered structure that has a low porosity compared to limestone, but dependent on the duration of the metamorphic process the size of the calcite grains can vary from fine to coarse. Metamorphic calcite with its crystalline uniformity, relative softness on quarrying and reflective properties has made them popular for statuary In its purest form, >98% CaCO₃, marble is pure white with
fluorescent properties. However as the lay term ‘marble’ suggests there are many variegated varieties with a range of colours, in the form of tints and veins, resulting from impurities present in the parent rock before transformation. The presence of small amounts of iron oxide or hydroxide produce red, brown and yellow hues whereas green coloration is produced by amphiboles, talc and serpentine. Organic material tends to give grey and black tints to the marble.

For statuary the highly coloured and veined marbles tend not to be used in preference for the purer whiter marbles. Historically and to the present day these have been predominantly quarried from Italy and Greece. In Italy, it is the Carrara region where the metamorphosed Jurassic limestone of the Apuan Alps produce Statuario (statuary marble); a coarse grained marble that is classed under three categories:

(I) First statuary (white statuary) – virtually pure white
(II) Second statuary – contains some grey markings
(III) Vein statuary – contains grey veining and markings

The classic Greek marbles were predominantly quarried from two sources

(I) Parian Marble – From the island of Paros, the marble has translucent highly reflective properties that not only found usage for statuary but also for the construction of the Parthenon in Athens

(II) Pentelic Marble – Quarried from Mount Pentelikon in Attica it is a white marble often with cloudy markings.

1.1.1.1 Calcite Mineral

Although limestone and marble form via different geological processes the basic building block of both rocks is the calcite mineral (CaCO₃). One of the most common and widely distributed of all the minerals, calcite is the
thermodynamically stable form of calcium carbonate with the two other main metastable polymorphs being aragonite and vaterite. In mineralogy, all minerals are characterised by a number of specific physical properties and a summary for calcite is given in Table 1.

<table>
<thead>
<tr>
<th>Mineral Physical Properties</th>
<th>Calcite Properties</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Trigonal</td>
<td></td>
</tr>
<tr>
<td>Colour</td>
<td>When pure colourless/white</td>
<td>Impurities can give grey, yellow, blue, red brown or black coloration</td>
</tr>
<tr>
<td>Form &amp; Habit</td>
<td>Highly vaned</td>
<td></td>
</tr>
<tr>
<td>Streak</td>
<td>white</td>
<td>Colour of the mineral powder</td>
</tr>
<tr>
<td>Lustre</td>
<td>Vitreous/pearly to dull</td>
<td>When pure fluoresces under UV</td>
</tr>
<tr>
<td>Cleavage</td>
<td>perfect rhombohedra {1011}</td>
<td>Powdered marble consists of minute cleavage rhombohedra</td>
</tr>
<tr>
<td>Hardness</td>
<td>3 Moh's scale</td>
<td>1=talc 10=diamond</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.715</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Physical properties of the calcite mineral.

The trigonal crystal system at its simplest can be visualised as a distorted halite structure (NaCl), where the Ca$^{2+}$ ions replace the Na$^+$ ion and the planar CO$_3^{2-}$ ions replace the spherical Cl$^-$ ion. This gives a rhombohedron unit cell as opposed to the cubic unit cell of NaCl. Figure 1$^5$. 
The crystal habit of calcite, which refers to the external shape that develops as an individual crystal or aggregate of crystals grow, is one of the most varied of all minerals. There are three main crystallised habits:

(i) Nail-head spar which is a combination of flat rhombohedron \{1012\} and prism \{1010\}

(ii) Dog-tooth spar which is a combination of scalenohedron \{2131\} and prism \{1010\}.

(iii) Rhombohedron \{1011\}

In addition to these main single crystal habits other crystalline habits include shapeless grains, fibrous crystals, lamella and stalactic and stalagmitic habits\(^6\).
Generally the metamorphically formed calcite is of the rhombohedron habit. When the strain in the crystal exceeds the elastic limit of the material as in the case of some physical weathering mechanisms the calcite crystal will cleave as a perfect rhombohedra \{1011\} and hence the association to sugar when weathered.

Marble being of high purity, especially sculptural marble, makes this calcareous stone susceptible to weathering by both natural and artificial mechanisms at a greater rate than has been observed with other stones. The next section reviews the mechanisms for the deterioration of marble sculpture.

1.2 Weathering Mechanisms for Calcareous Stones

As mentioned in the introduction the deterioration processes can be broadly categorised as physical, chemical and biological weathering and Figure 2, gives a summary of the factors that contribute to the three main types of weathering.

![Figure 2: Summary of weathering processes](image)
It is difficult to be specific about the mechanisms by which calcareous stone will decay, as its durability will depend on the chemical and physical structure of the exact stone and on the environment in which it is placed. Deterioration may occur through one or more of the main processes and within each category numerous weathering mechanisms exist. Therefore decay of stone materials is the result of the combined action of various phenomena, which may act independently or jointly, running consecutively or concurrently. This complexity makes it difficult to separate the mechanisms and current research has to be based on simplifying assumptions, so that a model may be produced which can explain the individual components of decay. For individual case studies, comparison to other research should be conducted with care since no two pieces of sculpture will have deteriorated identically.

For marble antiquities, most weathering mechanisms will have commenced as soon as the stone was quarried and sculpted. Over the last 150 years however weathering mechanisms have been predominated by anthropogenic gas action and this combined with the other decay processes has caused accelerated deterioration. Some of the more notable monuments that have suffered from accelerated weathering due to air pollutants include the Venetian marble buildings, the Parthenon in Athens and St Paul's Cathedral in London. During the late 18th century research into the causes and prevention of stone decay commenced and much of the early research, such as Schaffer's complete review first published in 1932, is still relevant.

The net effect of the decay processes for calcareous stone is the alteration of the surface. With continued ageing and exposure the stone loses its capacity to resist further decay until finally the ultimate form of marble deterioration occurs. This is the loss of all intergranular cohesion leading to the formation of 'sugary' individual crystallites.

Each category of decay is reviewed in detail, although as the complexity of weathering suggests there will be some overlap in the mechanisms.
1.2.1 Physical Weathering

Physical weathering encompasses the main effects of water and wind, which in combination with other elements such as particulate matter and temperature cycles form the basis of this type of erosion. It should be noted that water plays the primary role in the mechanisms of all modes of decay, (physical, chemical and biological), of both calcareous and any other stone. Without the presence of water there would be very little if any significant degradation of stone. A notable example of this is in the problem of hydration. An Egyptian granite obelisk, in pristine condition, was moved from Egypt to New York. Within two years large amounts of surface flaking was observed. Magnesium salts had gradually occupied the pores of the coarse grained granite by capillary movement as the monument lay prostrate on the delta sands of the Nile for 500 years. The salts did not re-hydrate until the monument was brought into high humidity. Hence the effect of water in whatever form cannot be underestimated.

1.2.1.1 Water Erosion

The effect of water on the deterioration of any stone is largely dependent on the stone’s porous nature. Porosity is defined as the ratio of the total volume of the pores to the total volume of the stone and takes the form of voids, pores or capillaries being either naturally present or formed as a consequence of corrosion processes. Freshly quarried marble normally has a porosity less than 3% compared to limestone and sandstone that varies between 5 – 25%. This would imply that as water is instrumental in most forms of decay marble would be more resistant to such attack, unfortunately this is not true. One of the major decay mechanisms of ‘new marble’ leading to an increase in porosity, and allowing for other forms of decay to initialise, is its susceptibility to changes in temperature, which leads to thermal cracking. Calcite has a peculiar thermal property, in that the crystal exhibits anisotropy such that the thermal expansion coefficient is dependent on the orientation within the crystal, Figure 3. Hence
as the marble is heated it expands in one direction and contracts in the other. The approximate unrestrained movement of marble for a thirty-degree change in temperature for pieces 1m in length is 0.15mm\(^2\). This movement causes internal stress on the marble that can result in the disruption of the crystal lattice, internal cleavage and detachment of crystals. Networks of interconnected cracks are created which propagate further on weathering\(^{13,14}\). Biscontin has reported that some marbles can increase to 50% overall porosity when exposed to temperature variations of 50°C\(^15\).

\[
C - axis
\]

\[
\begin{align*}
\text{Coefficient of thermal expansion} & \\
25 \times 10^{-6} \text{ m/m°C} & \parallel c-axis \\
-5 \times 10^{-6} \text{ m/m°C} & \perp c-axis
\end{align*}
\]

Figure 3: Thermal anisotropy of the calcite crystal

Freshly quarried and sculpted marble initially only show weathering affects on the very surface as water will have limited penetration. After centuries of air exposure the action of the original pores, thermal cracking and surface corrosion will result in the dramatic increase in porosity and hence allow water ingress allowing a multitude of mechanisms to occur.
Once marble begins to increase in porosity water can penetrate the stone by three main routes and is well reviewed by Camuffo\textsuperscript{16}:

I. \textit{Condensation of water vapour}, dependent on the chemico-physical characteristics of both the atmosphere and sculpture or monument.

II. \textit{Capillary rise} from the base of a sculpture or monument leading to dampness.

III. \textit{Rainfall}, which can significantly wet the surface and penetrate into the bulk.

I. Condensation is dependent on the surface temperature of marble. When the surface temperature drops below the dew point of the air, irrespective of the relative humidity (RH), a thin layer of water forms on the surface. The reverse process, evaporation, occurs when the temperature of the surface is greater than the wet bulb temperature of the air and can be aided by; (i) the continual supply of water from the interior by the action of capillary movement as the water on the surface is removed. (ii) By the temperature of the air (as it increases so does the rate of evaporation). (iii) By the rate of flow of air over the surface, (as the wind speed increases so does the rate of evaporation). For a porous material as with the case of weathered marble the process is complicated by the individual pore characteristics, which also affect the rate of condensation.

The process can be summarised. As interstitial condensation occurs the internal surfaces are progressively covered with a layer of water that is bound to the surface and comprises of a few monomolecular layers. Continual condensation increases bulk free water within the pores until theoretically all of the pores are filled and the interior is saturated (and moisture forms on the surface). Evaporation may then occur from the surface when the temperature of the air is higher than the surface, and when the RH is lower than that in the pores. The rate of evaporation will increase with increased flow of air over the surface provided that water can move to the surface quick enough to compensate for
the loss. If this occurs then the surface will also remain wet during evaporation allowing for the action of many decay mechanisms\textsuperscript{17}. If the water moving to the surface is insufficient to compensate for the loss by evaporation, (often due to the size, shape and form of the pores that effect the RH), the surface will dry and the evaporation rate decrease. Therefore as in the case of marble, that is relatively dense, the surface may dry before all the pores have emptied meaning that below the surface the marble is still saturated, which allows for weathering mechanisms to still occur due to the actions of salts and freeze/thaw cycles.

II. Capillary action is the main form of transportation of water through marble. The action of capillary rise is a consequence of surface tension and can be described by the Laplace equation:

$$h\rho g = \frac{2\gamma}{r}$$

\textbf{Equation 1 Laplace Equation}

Where $h$ is the height of the column of liquid, $g$ is the specific gravity, $r$ is the radius of the capillary and $\rho$ and $\gamma$ are the density and surface tension of the liquid respectively. Therefore the pressure under the meniscus is less than that due to the atmosphere by an amount $2\gamma/r$ and hence the external pressure presses the liquid up the capillary. The capillary force will increase as the pore diameter decreases and when they are sufficiently small the forces of gravity are overcome and ground water may ingress into the sculpture. The progressive displacement of water ensures that nothing stops the ingress of water unless the capillary end becomes blocked, which can lead to pressure exertions. This is therefore much more efficient in causing dampness than by the process of condensation\textsuperscript{18}.

III. Rainfall is the most important source of water to vertical faces of sculptures and monuments and again is dependent on climatic factors and the material. The action of the rain can aid external weathering by washing off the alteration products of chemical decay, creating fresh surfaces for further decay, as well as
wetting the surface and bulk material which can lead to many forms of physical
decay. In addition rain can act as an intermediate in weathering carrying
dissolved acid gases to the surface.

Once the stone is wetted the main processes of physical decay are believed to include:

(I) Freeze/thaw cycles.

(II) Soluble salts: including migration, hydration and 
     re-crystallisation.

(III) Dissolution and leaching of calcite minerals. 
     (referred to in the chemical weathering of marble)

(I) Freeze/thaw cycles is one of the main physical weathering mechanisms 
    reported in the literature. Large mechanical stresses can be exerted within the 
    stone when the temperature of the marble drops below freezing. This is caused 
    by water in the pores forming ice which as a consequence expands by up to 
    10%¹⁰. The hydraulic pressure that occurs at -5°C is approximately 50 MN m⁻² 
    (500 atm) where the compressive strength of porous stone is approximately 7.5 
    – 56 MN m⁻²¹⁹. Damage will only occur if the pores are nearly or completely 
    filled with water and the level of importance placed on this mode of decay in 
    the literature is most probably excessive.

(II) Soluble salts are arguably the most prevalent form of physical weathering. 
Salts can be present in the stone either naturally as impurities during the rock 
formation or by accumulation from ground water, air pollution, atmospheric 
aerosols, (such as marine areas, like Liverpool, rich in NaCl), deposits from 
organic vegetation and animals, chemical alteration and poor conservation 
methods. Typical salts that accumulate in the stone include chlorides, sulphates 
and nitrates of Na, K, NH₄, Mg and Ca¹¹,²⁰. Dependent on the distribution of 
the salts, they can exert physical weathering at the surface, and in the pores of 
the material. This distribution of crystallised salts is referred to as efflorescence 
and subflorescence, Figure 4.
The salts, which have varying degrees of solubility, can initially be spread throughout the material. As a result of evaporation of water from the surface, migration of the salt solutions by capillary movement also occurs and they tend to become concentrated towards the surface. At and near the surface the salts are repeatedly dissolved and re-crystallised as a result of wetting and drying cycles. If the evaporation rate is high the salts will crystallise on the surface resulting in white patches or coloured stains, depending on the type of salt. This is known as efflorescence. When the rate of evaporation is greater than the rate of capillary movement of the water the interior is dried and salts crystallise below the surface resulting in subflorescence. Additionally changes in the relative humidity can also cause salts to crystallise from solution. Nitrates crystallise at 25°C if the relative humidity falls below 50% and chlorides at 25°C for a relative humidity below 30%. This can cause the loss of cohesion.
due to re-crystallisation and salt hydration pressures. The re-crystallisation of salts can exert large pressures under the surface eventually leading to crumbling and shattering of pieces of stone due to differences in density between the two phases. It has been calculated that a 10% solution of NaCl will provide enough energy to overcome the mechanical strength of calcite in marble. Salts can also become hydrated under the fluctuating influence of temperature and humidity. When crystallised the hydration pressures can easily be in excess of those required to overcome the cohesive forces of the rock. Winkler, postulates that as CaSO$_4$·1/2H$_2$O hydrates to CaSO$_4$·2H$_2$O a pore pressure of 2190 atm can be produced. When this occurs below the surface weakened marble will shatter off.

The actions of such salts are common to marble antiquity. Weathering of ‘The Arch of Galerius’ in Salonica is attributed to the cumulative effects of physical processes. Thermal cycles and the corrosive marine environment have allowed the ingress of chloride salts, which along with the cold winters has led to large loss of sculptural detail. The marble buildings within the Acropolis in Greece give a good example of how improper conservation has led to the destructive action by soluble salts. Restoration took place between 1902-1909 to anchor the marble blocks, achieved by the installation of reinforcing iron bars. Subsequent oxidation of the iron caused the oxidation products (limonite) to migrate towards the surface under capillary action. Surface efflorescence has led to the formation of brown stains. Subflorescence, where the products crystallise with a larger volume due to reduction in density has caused the loss of large amounts of material. Today the action of this restoration is the largest decay problem of the marble buildings within the Acropolis.
1.2.1.2 Wind Erosion

Wind erosion (corrasion) is when abrasive particles impact on the stone’s surface with enough force to cause micro mechanical damage which on prolonged exposure results in macroscopic effects\textsuperscript{16}. Not all particulate matter causes damage, corrasion is dependent on the wind speed and the size and density of the particle. If a particle has a diameter $d < 100 \mu m$ it is a fine dust that has no effect in abrasion but is significant in surface soiling. Medium sized particles in the range $100 < d < 600 \mu m$ are temporarily lifted by the action of the wind by a process known as saltating and are effective in terms of erosion at the base of the monuments. Particles with $d > 600 \mu m$ are too large to be lifted by the action of wind. It is extremely rare to observe corrasion in urban areas as the density of buildings reduces the wind speed and the size of particulate matter tends to be too small to cause any damage. It is, however, the most important mechanism of decay in dry and sandy regions such as Egypt were cases such as the Great Sphinx show severe signs of wind erosion. Therefore the action of the wind may have the final hand in the deterioration of marble statuary but the actual processes of physical decay are more attributed to the action of water\textsuperscript{16}.

1.2.1.3 Soiling by Particulates

In general particulate matter does not directly cause accelerated decay of calcareous stones, it is more synonymous with the soiling of surfaces by the formation of dirty crusts in sheltered areas. The condensation layers present on the surface and in the pores of the stone are efficient collectors of particles. Particles that impact on the wet surface tend to ‘stick’ without bouncing, where they become incorporated into the gypsum layer. Sabbioni’s study of black crusts, from marble exposed in Ancona, Italy, found that approximately 20% of the surface layer was comprised of particulates emanating from various sources\textsuperscript{23}. Average size and composition is used to classify the particulate matter. Large particles >10 \mu m mass median aerodynamic diameter (mmad) are normally comprised of soil materials, re-suspended road dust and marine
aerosols. Medium particles, < 2-3 \mu m_{\text{mmad}}, are dominated by sulphates and tend to be acidic. The smallest particles < 1 \mu m_{\text{mmad}} are comprised of carbonaceous material, such as soot and fly-ash and is generally accepted as the principle component of airborne particulate matter, with carbon comprising 10-20% of aerosol mass\textsuperscript{34}. It is reported that in urban areas over 70% of particulate matter are produced due to the activity of man\textsuperscript{24}.

The formation of dirty areas is a result of the geometry of the surface and its exposure to washing. Three zones tend to exist:

(I) White zones, where the stone is continually washed by the action of rain and any particulate deposited will be removed and can increase the recession rates by mechanical action by pulling stone off due to the strength of bonding.

(II) Grey zones, where the surface of the stone is protected from the rain and is generally dry, the colour is the result of deposited dust and represents no damage.

(III) Black Zones, where the stone is frequently dampened by rain and condensation but the adhered particles are not washed out by rain. This is indicative of areas of friable calcareous stone existing under a hard crust of gypsum.

As well as causing the loss in aesthetic appeal it has been suggested in a number of reports that carbonaceous material will have a catalytic effect on the reaction of acidic species at the surface\textsuperscript{16,25,26}.

1.2.2 Biological Weathering

Monuments and sculptures in damp and humid environments provide ideal locations for the support of biological life that can lead to biological weathering\textsuperscript{27,28} A water threshold exists above which growth of various types of organisms such as algae, lichens, bacteria, fungi and higher plants can occur.
Biological action can result in mechanical damage, chemical reaction and colour alteration.

Typical mechanical action is the damage caused by the effect of roots and hyphae that embed and penetrate into cracks and pores already existing in the stone. Forces exerted by their action can further weaken the stone and can lead to structural damage and surface pitting\textsuperscript{10,29}.

In terms of chemical alteration, lichens (symbiotic algae and fungal growth) act upon marble in two ways. (i) By secreting organic acids such as oxalic acid that react with calcium carbonate (ii) By retaining water and hence keeping the marble wet, which can facilitate other weathering mechanisms\textsuperscript{11}. Lichens however, tend not to be found in highly polluted atmospheres due to their inability to survive in the presence of high concentrations of SO\textsubscript{2}(g). In contrast some bacteria are able to thrive in atmospherically polluted areas, and bacteria have been found in all samples taken from the Acropolis, Athens\textsuperscript{29}. Two main classes have been shown to be prevalent in the chemical alteration of marble where these are nitrogen and sulphur fixating bacteria. For example thiobacilli can synthesise sulphuric acid from sulphur dioxide leading to the formation of calcium sulphate\textsuperscript{30}. How much the bacteria contribute to the overall chemical alteration of marble is still the subject of much research.

Finally, it has been shown that biogenic growths are responsible for many of the colour alterations observed on the surface of weathered marble\textsuperscript{31,32}, rather than discoloration due to atmospheric particulate deposition only. The colours cover the whole visible spectrum from clear white to black. The most commonly observed colours attributed to biogenic action are beige-grey, orange-brown, red-brown to black and green to black. These colours are generally ascribed to the metabolism of fungi and some bacteria, which produce polyphenolic substances of melanin and humic groups.
1.2.3 Chemical Weathering

The vulnerability of calcareous monuments and sculptures to chemical weathering by acidic air pollutants is reportedly the most aggressive mechanism over that of physical and biological decay. The acceleration in stone deterioration caused by pollutant action is more severe than natural weathering as is evident from comparison of statues and monuments in rural sites to those in polluted urban areas. It is widely accepted that much of the damage to ancient monuments has occurred in the last 150 years due to the increase in anthropogenic pollutants derived from the products of combustion. The pollutants are presented initially in the atmosphere as either gases or particulates. The acidic gases cause the chemical alteration of calcite at the surface whereas the particulates are important in surface soiling and were reviewed in the physical weathering mechanisms.

1.2.3.1 Atmospheric Gases

The acidic gases of most importance in the accelerated deterioration of marble and limestone are: Sulphur dioxide (SO₂), nitrogen oxides (NOₓ), and both their oxidised products, and hydrogen chloride (HCl). Carbon dioxide, (CO₂), is also a weathering agent but is less important in accelerating decay. It was however, the predominant, aggressive agent in pre-industrial times and its action can be considered as the natural rate of chemical weathering. The composition of dry air is shown in Figure 5.
ATMOSPHERIC GAS COMPOSITION

There are numerous trace gases in the air, which comprise less than 0.004% of the total air concentration. Included amongst these are the acidic gases $SO_2$, $NO_2$, and NO. These trace gases are predominantly the result of emission from natural sources such as volcanic activity, and as such are thought not to contribute significantly to accelerated weathering. Man-made pollutants are raising atmospheric trace gases and $CO_2$ levels above that of the natural concentration. $SO_2$ increase is attributed primarily to the burning of oil and coal, and $NO_x$ increase is thought to be a result of escalating exhaust emissions\(^\text{34}\). When considering total atmospheric gas concentration, the anthropogenic levels of gases are minimal compared to the same gases produced naturally, implying that the deleterious effects should be insignificant. However, most of the anthropogenic gases are produced in dense urban areas where most statuaries and monuments are located, giving concentrated ‘pockets’ of acidic gas. These species are highly reactive towards...
calcite and hence any amount above the background level will accelerate decay.

The acidity contributed by the main corrosive gases have been calculated for Europe with the UK figures being $\text{SO}_2 : 71\%$, $\text{NO}_x : 25\%$, $\text{HCl} : 4\%$.

Hence the order of importance of the trace gases in accelerated decay of statuary is assumed to be:

$$\text{SO}_2 > \text{NO}_x > \text{HCl} > \text{CO}_2$$

Removal of these pollutants from the atmosphere and subsequent deposition onto the calcareous stone is generally referred to by two main mechanisms:

(I) Wet Deposition. The transport of the gases to the surface occurs as the result of acid rain. The pollutant gases are scavenged from the atmosphere and dissolved by water droplets. The dissolved gas is then oxidised, which can occur via a number of mechanisms e.g. for $\text{SO}_2$, via heterogeneous oxidation in the droplets by (i) $\text{O}_2$ in the absence of catalysts, (ii) $\text{O}_2$ in the presence of a catalyst, (iii) By the presence of strongly oxidising agents. Cloud transportation then moves the pollutant until wash out occurs as rain which results in the deposition of acidic species.

(II) Dry Deposition, is defined as "the aerodynamic transfer of atmospheric trace gases and particles to the surface not associated with the fall of hydrometeors (rain)"34, i.e. direct exchange between the atmosphere and the surface. The role of water is still believed to be crucial, in the form of multilayer surface adsorption, which helps overcome surface resistance in the deposition of certain gases e.g. $\text{SO}_2$. The gases are then believed to be dissolved in the moisture layer to form acidic species which react with the surface.

A summary of the action of the individual gases is given below.
1.2.3.1.1 Carbon Dioxide

Carbon dioxide, has always been part of the planet’s atmosphere and although its concentration has increased its adverse effect on marble monuments is considered to be the natural decay rate. Simulation experiments have been conducted by Guidobaldi and Mecchi\textsuperscript{33}, on the recession rate of marble in pre-industrial times and have reported it to be dependent on two parameters; rainfall quantity and intensity. Increase in quantity and decrease in intensity giving a higher recession rate. The recession rate on a vertical, partially sheltered area of Carrara marble is in the range 0.03-0.05 mm per century whereas in unsheltered regions is 0 15-0 25 mm per century when 500-800 mm of rain falls per annum (typical annual rainfall in Rome). This assumed a pH of 5.6, which corresponds to the equilibrium between rainwater and atmospheric CO\textsubscript{2} (0 032\%\textsuperscript{38,37}. The well documented dissolution of CO\textsubscript{2(g)} in rainwater results in the formation of carbonic acid:

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq)
\]

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(aq)
\]

\[
\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-
\]

The weak acid can react with calcite to form the much more soluble calcium bicarbonate

\[
\text{CaCO}_3(s) + \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{Ca(HCO}_3)_2(aq)
\]

It should be noted that less than 1\% of the dissolved gas actually forms carbonic acid and so the detrimental effect is not believed to be large. As the acidity of rain increases, normally due to the formation of acid rain by the dissolution of SO\textsubscript{2(g)} or NO\textsubscript{2(g)}, the recession rate has been estimated to rise sharply as shown in Figure 6 overleaf. This does not however account for the dependence on rainfall quantity and intensity. If contact between the water and surface is not maintained for relatively long periods a pH lower than 4.5 does not have a significant effect\textsuperscript{33,38}. 
1.2.3.1.2 Sulphur Dioxide

SO$_2$(g), is the species most associated with stone damage this century. The interaction of any pollutant gas with the stone surface entails a number of considerations, the most important are believed to be:

- Concentration of the species in the atmosphere
- Aerodynamic factors such as wind velocity, speed and direction with respect to the surface, humidity and incident rainfall.
- Surface resistance.

The typical concentration of SO$_2$(g) in the atmosphere is variable depending on location and Lipfert, reconciles many experimental findings from around the world to give a broad overview$^{39}$. Values quoted range from 20-100 $\mu$g m$^{-3}$, with a total mass of between 2-3 $\mu$g cm$^{-2}$ day$^{-1}$ actually reaching the surface, which equates to approximately 20 monomolecular layers.

Figure 6: Recession Rate of Marble as a Function of Rain Acidity$^{33}$
Studies of the wet deposition of SO$_2$ as H$_2$SO$_4$(aq) have shown that the pH of acid rain can vary from 3.5 - 5.0$^{33,38,40,41}$. The average composition of acid rain in a UK city in terms of sulphate, nitrate and chloride content have been monitored as 8.64, 3.1 and 5.15 µg mL$^{-1}$ respectively with a typical rainfall of 800 mm per annum$^{42}$. This corresponds to an average presentation rate of 21.9, 7.68 and 13.1 x 10$^{-6}$ µg cm$^{-2}$ s$^{-1}$, respectively. The theoretical, field and laboratory based SO$_2$(g) effect on recession rate has been reported in the literature and ranges from 0.2-3.5 mm per century for marble$^{33,39}$, the variability depending on the aerodynamic factors, the concentration of SO$_2$ and the type of stone.

A proposed mechanism for the wet deposition begins with the oxidation of SO$_2$(g) in atmospheric water droplets, Figure 7.

\[
\begin{align*}
\text{SO}_2(\text{g}) + \text{H}_2\text{O} & \leftrightarrow \text{SO}_2\text{H}_2\text{O} \\
\text{SO}_2\text{H}_2\text{O} & \leftrightarrow \text{H}^+ + \text{HSO}_3^- \\
\text{HSO}_3^- & \leftrightarrow \text{H}^+ + \text{SO}_3^{2-} \\
\end{align*}
\]

*Figure 7: Proposed mechanism for atmospheric oxidation of sulphur dioxide$^{36,40}$.*

Where SO$_2$ H$_2$O is the physically dissolved SO$_2$, HSO$_3^-$ is the bisulphite ion and SO$_3^{2-}$ is the sulphite ion. The oxidation could proceed via a number of possible mechanisms as mentioned earlier to give the acidic sulphate species$^{36,40}$.

\[\text{SO}_3^{2-} + \text{oxidising agent with or without catalyst} \leftrightarrow \text{SO}_4^{2-}\]

The acid rain formed reacts with calcite to form calcium sulphate dihydrate, which in exposed areas will be removed by further rainfall causing recession:

\[\text{CaCO}_3 + \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + \text{CO}_2\]
For ‘dry deposition’ the main controlling factors affecting surface deposition on calcareous stone, are; surface roughness, shape, wind speed, atmospheric turbulence, and surface wetness. These have been categorised as two resistances to deposition: (i) the aerodynamic resistance and (ii) the surface resistance, when both are favourable deposition will occur. Experimentally, the role of these resistances is determined by the deposition velocity \( V_d \). The deposition velocity is an overall mass transfer coefficient, which is equal to the average rate of migration of a dilute gas towards an absorbing surface\(^{43,44,45}\). Typical values reported for \( V_d(\text{SO}_2) \), for calcareous stone, are in the range of 0.3-1.3 cm s\(^{-1}\). This corresponds to a typical presentation rate of 0.35 - 1 \( \mu \text{g cm}^{-2} \text{day}^{-1} \). Somewhere between 0.5 - 10% actually reacts depending on the relative humidity and amount of surface wetness\(^{46,47}\).

The interaction of \( \text{SO}_2(\text{g}) \) with the calcite surface is known to result in the formation of gypsum (\( \text{CaSO}_4.2\text{H}_2\text{O} \)). The exact physico-chemical surface reaction is still not fully understood and the reaction mechanism normally suggested is shown in Figure 8.

\[
\text{CaCO}_3 + \text{SO}_2(\text{g}) \overset{\text{H}_2\text{O}}{\rightarrow} \text{CaSO}_4.1/2\text{H}_2\text{O} + \text{CO}_2 \quad \text{CaSO}_4.2\text{H}_2\text{O} + \text{CO}_2 \overset{\text{O}_2}{\rightarrow} \text{CaSO}_4.2\text{H}_2\text{O} + \text{CO}_2
\]

**Figure 8:** Proposed reaction of calcite with sulphur dioxide deposited under ‘dry deposition’ conditions\(^{48,49,51}\)

The extent of the reaction is influenced by the role of surface water, chemical buffering within the moisture layer and the presence of catalysts and oxidants. When the stone is considered to be dry, relative humidity is believed to influence the deposition of \( \text{SO}_2 \) and subsequent reaction with calcite. A relative humidity of 84% is reported to produce a very thin moisture film (2nm) on the surface and in the pores, however at a relative humidity below 50% there will
be no moisture film on the surface of the stone. Experimental results have shown that there is no significant reaction below 50% RH, but at 84% RH approximately 1-2 5% of the SO₂ reacts to form gypsum on Pentelic marble. Work by Elfving, Hutchinson and Johansson suggest that in the presence of a thin moisture film the SO₂ is adsorbed onto the surface and reacts to form a surface sulphite intermediate. This intermediate is then further oxidised to form gypsum.

When the surface pores are wet from condensation and capillary action a moisture film thickness of approximately 0.2 mm can form and the percentage reaction with SO₂ rises to between 2.4-10%. The increase in the volume of water will tend to favour dissolution of the SO₂ and hence formation of H₂SO₄, leading directly to gypsum formation.

It is well known that in sheltered regions the formation of gypsum via either of the mechanisms outlined above can accumulate on the surface forming gypsum crusts. These crusts can act as a physical barrier to further decay although crust thickening has been suggested to occur by the release of Ca²⁺ ions below the surface, which migrate through the layer where they react with more SO₂. The leaching of Ca²⁺ ions is believed to be due to the attack of H⁺. The initial formation of gypsum is thought to preserve the surface relief, referred to as boxwork. This hardened crust may give the appearance of solidity, however, under this the calcareous stone will have large cavities formed by the migration of Ca²⁺ ions. This results in lack of crystal cohesion and the formation of friable stone as summarised in Figure 9.
1.2.3.1.3 Nitrogen Oxides

NO$_{x(g)}$ is present in the atmosphere as nitrous oxide (N$_2$O), nitric oxide (NO) and nitrogen dioxide (NO$_2$). The oxidation of these gases leads to the formation of nitrates the most important being nitric acid (HNO$_3$). Typical concentrations of NO$_2$, NO and HNO$_3$ and their deposition velocities in an urban environment have been calculated for wet zinc$^{34}$, (which is reported to be comparable to limestone), and are shown in Table 2.
NO, NO₂ and HNO₃ are the primary and secondary pollutants from the photochemically controlled effect commonly known as 'Los Angeles smog', which is found to depend on the season and is most predominant in the summer months. Similar phenomena are commonly observed in Athens where atmospheric concentrations are similar to those in L.A. From Table 2, the $V_d$ values obtained for NO and NO₂ are approximately 10% less than the deposition velocities for SO₂ ($V_d$ 0.3-1.3 cm/s)⁵⁴. This has been attributed to the surface resistance of the calcareous stone. Both NO and NO₂ are not greatly soluble in water and hence for wet surfaces will either deposit very slowly as for NO₂ or negligibly as for NO. Published results have indicated that the deposition of NO₂ onto stone surfaces is believed to be more important in acting as an oxidising agent for SO₂ than in the formation of Ca(NO₃)₂⁴⁶. It is reported that HNO₃ produced under photochemical smog conditions can result in surface nitrate species, (unlike its parent gases, HNO₃ deposits with minimal surface resistance) Haneef et al⁵⁵, have presented the possible mechanisms for the formation of HNO₃ and these are reproduced in Figure 10.
The formation of calcium nitrate is not normally retained on the surface as it is highly soluble in water. This action will therefore lead to the recession of the stone.

1.2.3.1.4 Hydrogen Chloride

HCl anthropogenic emissions arise primarily from the burning of fuels. Coal is the largest single source of HCl emissions in the UK. The mean Cl\(^-\) ion content of British coal is 0.23% with 94% of this likely to be emitted as HCl in stack gases. The reported total annual HCl emissions in the UK from anthropogenic sources has been quoted as 260 kt a\(^{-1}\). The concentration of HCl in urban areas has been quoted between 0.2-3 µg m\(^{-3}\) to as high as 14-50 µg m\(^{-3}\).
HCl is a highly reactive gas that is quickly removed by most surfaces particularly if they are moist. The deposition is similar to that of HNO₃ in that it experiences minimal surface resistances only the aerodynamic resistances such as air turbulence. Laboratory based results for the action of HCl on moist calcareous stone under dry deposition has shown it to be more readily absorbed than SO₂ due to its greater solubility. HCl reacts rapidly with calcite to produce a soluble product CaCl₂, which would be readily washed away from the surface.

\[
\text{CaCO}_3 + 2\text{HCl} + 6\text{H}_2\text{O} \rightarrow \text{CaCl}_2\cdot6\text{H}_2\text{O} + \text{H}_2\text{CO}_3
\]

Realistically, the concentrations of HCl in most urban areas are relatively small compared to SO₂ and its high deposition on any surface and ready scavenging by rain, means that only monuments and statues ‘close-to-source’ will be affected by its action.

\[1.3\text{ Summary}\]

Sculpture that has survived many hundreds of years of weathering have over the last 150 years deteriorated at an accelerated rate. Direct correlation to the increase in atmospheric pollutants and detailed study of stone surfaces have given an indication of the factors that cause deterioration. Once deposited on the surface, the acidic species readily react with CaCO₃ forming alteration products. These can be either washed away if formed on unsheltered surfaces exposing a fresh surface for further reaction resulting in the recession of the marble and hence loss of sculptural detail. If deposition occurs in sheltered regions there will be an accumulation of the reaction product, primarily gypsum (CaSO₄·2H₂O), which forms crusts that can act as a physical barrier to further attack but will tend to have desegregated calcite crystals below the surface, weakening the sculpture. Combined with the other effects of
of weathering the marble will become highly friable and eventually lead to the loss of material and sculptural detail.

In order to preserve the sculptures and monuments for many more centuries it is important to undertake conservation measures in terms of cleaning, consolidation, and preservation. Research in this area is as large as the study of weathering mechanisms and the following chapter reviews methods in conservation.
Chapter 2 RESTORATION AND CONSERVATION

When conserving any stone artefact from a small marble sculpture to a limestone cathedral the physical processes involved follow a similar pattern. Firstly, cleaning is undertaken to recreate the original aesthetic appeal as well as removing potentially damaging catalysts in the dirt layer. Once the surface of a stone has been cleaned this exposes a decayed or fresh surface, which if placed back into its original environment, could decay more rapidly than before cleaning. It is therefore essential that the surface be consolidated i.e. rebind the friable material thus restoring the cohesive forces of the individual crystallites. As water is important in accelerated weathering a preservation treatment will also be required to form a protective coating against further water absorption. Stone conservation processes are therefore traditionally classified under three main headings:

1. Cleaning
2. Consolidation
3. Protection

Often considered together

2.1 Cleaning Methods

Particulate matter can be strongly bound to the surface of stone by intermolecular forces such as electrostatic, Van der Waals forces and hydrogen bonding. Although weaker than ionic or covalent bonding the bonding energies exhibited can be great enough to cause significant difficulty in removal of dirt particles. If the wrong method is used this can lead to irreversible damage, especially with friable material often existing beneath these layers.
A number of general criteria exist when determining the technique to be employed:

- Cleaning must not directly or indirectly damage the stone.

- Preservation of the patina must be maintained i.e. The original gypsum layer that conserves the surface relief of a sculpture (box work).

- No harmful by-products should be produced that may lead to future accelerated weathering.

- The cleaning technique must be sensitive so that cleaning can be controlled accurately.

- The result of the process must give a clean, smooth surface that has not increased overall porosity.

There are five general cleaning methods available for the removal of dirt from stone and a brief description of each is given:

1. Water-based methods
2. Mechanical methods
3. Chemical methods
4. Poulticing
5. Laser cleaning

2.1.1 Water-based Cleaning

Water is a cheap, non-hazardous material with high polarity and will remove soluble salts not touched by organic solvents. Water cleaning may be applied via a sprinkling technique which continues until the dirt is softened enough to allow removal by scouring and rinsing. A more vigorous technique is by firing a jet of water onto the surface for a sufficient period to weaken the adherence by swelling the dirt layer. Again the method requires scrubbing to remove the dirt followed by rinsing with more water. These methods have been used for
the removal of soluble salts on limestone, however the large amounts of water employed can lead to penetration in depth which could result in aiding salt recrystallisation and freeze/thaw cycles.

The final water based method is steam cleaning under pressure. This uses minimal water and can remove dirt mechanically. It is not advisable to use this method on sculptures believed to be friable under the dirt.

2.1.2 Mechanical Cleaning
Abrasive methods are the most common of mechanical techniques and work by cutting away deposits of stone with sharp particulates that are carried in a jet of air. The three main methods being: Wet grit blasting, which involves blowing a mixture of water and abrasive at the surface. Dry grit blasting which uses only the abrasive in a stream of air or micro-blasting which is essentially the same as dry grit blasting, only, using microscopic particles of aluminium oxide in a jet of air. The first two methods are inadvisable for use on monuments and sculptures due to their lack of control and destructive action. Micro-blasting is quite a valuable technique, but only in skilled hands.

2.1.3 Chemical Cleaning
Chemical cleaning has in the past been used to remove dirt from calcareous materials although this practice is rarely continued today. Chemical cleaning utilises acids and acidic salts that function by reacting with the black crusts to dissolve them, however control over their movements once on a surface especially a porous surface can lead to reaction of the bulk material.

Organic solvents can be used on a small scale by application with cotton wool swabs. Typical solvents include mixtures of acetone or white spirit with water, and methylene chloride. However careless use in unskilled hands can lead to damage in the bulk of the stone.
2.1.4 Poultice Cleaning

A paste or poultice acts by providing a medium that draws out the dirt. An example is a water poultice, which is used on marble. The poultice normally comprised of de-ionised water and magnesium silicate is pasted over the surface effectively suspending the water and allowing the dirt to be dissolved. As the poultice dries the water evaporates so drawing the dirt to the surface, the poultice once dry falls away from the marble and the dirt can then be removed by washing with deionised water.

2.1.5 Laser Cleaning

The difference between laser cleaning and all of the previous cleaning methods described is its non-invasive action. The principle of the method is the selective vaporisation of dirt particles from the surface, without the removal of any of the original material. This will occur due to the fact that coloured particles will absorb a large proportion of the incident laser radiation which may be sufficient to cause vaporisation i.e. black pigments will absorb most of the laser radiation whereas white pigments will reflect most of the radiation. Therefore, with careful control, it is possible to remove individual dirt particles from a white surface without causing damage to the clean areas. Research at Loughborough University identified a Nd-YAG Q-switched laser to be the most efficient laser in the removal of dirt crusts from a variety of stones including friable marbles, limestones, sandstones and even terracotta which will naturally have a high absorbency of incident laser radiation.
2.2 Consolidation Techniques

If the stone has become friable, then some form of consolidation is required to strengthen the weakened areas. Many criteria for the role of consolidants have been proposed over the years and C. Price in his Overview of Current Research summarises the enormity of such criteria for one process.

*It all sounds so easy. One just has to find something that will penetrate the stone, binding it together and securing it onto the sound stone beneath. And why stop there? Perhaps it could embed the salts and prevent further cycles of crystallisation or hydration. Or perhaps it could make the surface of the stone water-repellent, so it will resist acid rain. Of course, the treatment will need to be reasonably cheap, easy to apply, and safe to handle. It will need to remain effective for decades at a time, in order to last from one maintenance cycle to the next. The treated stone will need to have much the same moisture expansion, thermal expansion and elastic modulus as the untreated stone, in order to avoid internal stresses. Ideally the treatment should work equally well on any type of stone, regardless of the cause of decay. And — I nearly forgot— it must be completely invisible.*

The only criteria, and maybe the most controversial, missed from his summary is that all consolidation treatments should be reversible. Although he and others generally accept that reversibility is an ideal rather than actually feasible Hence besides consolidating friable material, issues such as durability, depth of penetration, effect on stone porosity, effect of moisture transfer, compatibility with the actual stone, the resulting effect on the appearance and future consolidation methods must be considered. Unfortunately a universal consolidant has not been found and there have been numerous attempts throughout history to try and prolong the lifetime of monuments and statues and only a few of the major and more recent techniques of the many hundreds are described
Generally consolidants can be classed under two categories:

1. Inorganic methods – General aim is to chemically precipitate inorganic material capable of adhering to the stone mineral

2. Organic / polymeric methods – To produce an organic ‘adhesive’ between the grains that have lost cohesion.

### 2.2.1 Inorganic Consolidation

Inorganic stone consolidants were developed extensively during the mid to late 19th century after a Royal Commission was implemented to study the decay of stonework at the Houses of Parliament\(^{10}\). Many were developed from existing decorative and preservative methods dating back many centuries.

Such inorganic methods include the use of barium hydroxide solutions (baryta), alkali silicates, and lime methods.

#### 2.2.1.1 Barium Hydroxide (baryta)

Barium hydroxide or baryta, was first proposed as a stone preservative for marble and limestone in a number of patents during the 19th century. The objective of the barium treatments was either:

(I) To convert the alteration product calcium sulphate into the less soluble barium sulphate, which was first proposed by Church in 1862\(^{60}\). Where the barium sulphate forms an insoluble barrier to further calcite conversion.

(II) To deposit barium carbonate into the friable material to try and consolidate the stone and immobilise salts by the application of barium hydroxide. This was the subject of patents by Ransome\(^{61}\) in 1856 and Dennstadt\(^{62}\) in 1884, who further suggested repeated saturation of the porous stone with a hot solution of barium hydroxide followed by drying and carbonation under a carbon dioxide atmosphere. He also suggested ‘sealing’ the surface by the formation of insoluble barium or strontium sulphate or chromate, by first brushing the surface with either sulphuric or chromic acid, followed by the saturation with solutions of either barium or
strontium hydroxide. Church later recommended successive applications of barium hydroxide, each with a drying cycle, to precipitate barium carbonate into the sandstone, marble or limestone fabric and it is this process that is commonly referred to as the Church process.

Although initially producing an effect on the stone it was later found that only surface hardening occurred, often with a colour alteration and eventual exfoliation of this layer. The causes have been attributed to poor penetration of the solutions leading to surface precipitation only, which in turn leads to an impenetrable layer. Also the molar volume difference between the original calcite and the barium carbonate and sulphate mineral could be a cause of exfoliation.

During the late 1960s and early 1970s in trying to address the lack of penetration by the original methods, both Lewin and Baer and Sayre have reported deep consolidation of marble and limestone by the use of homogeneous solutions. Homogeneous in that the material to be precipitated and the precipitating chemical are both present in the same solution.

Lewin and Baer, suggest the use of a hot barium hydroxide solution containing 10% urea in water (or a water-glycerine mixture if left for a longer period), such that the urea provides the carbonate source, Figure 11.

\[
\begin{align*}
\text{CO(NH}_2\text{)}_2 & + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + 2\text{NH}_3 \\
\text{Ba}^{2+} + \text{CO}_3^{2-} & \rightarrow \text{BaCO}_3 \\
\text{Ba(OH)}_2 + \text{CO(NH}_2\text{)}_2 & \rightarrow \text{BaCO}_3 + 2\text{NH}_3
\end{align*}
\]

Figure 11: Reaction equations postulated by Lewin

Lewin reported that under both laboratory conditions and field conditions there was no tendency for spalling or flaking of the hardened surface.
Evaluation of the barium hydroxide-urea method by Schnabel\textsuperscript{68} in 1992, reported that the method was not suitable for marble consolidation in-situ as opposed to the test results published by Lewin where samples were immersed in the solution. No consolidatory effect was observed.

In Sayre’s method for limestone, barium sulphate as opposed to barium carbonate is deposited from a homogeneous solution within the porous stone. Here an aqueous solution of a barium (or strontium) salt of a monoester of sulphuric acid is slowly hydrolysed to barium sulphate, which is more chemically inert and insoluble, Figure 12.

\[
\text{Ba(C}_2\text{H}_5\text{SO}_4)_2 + \text{Ba(OH)}_2 \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{BaSO}_4
\]

Figure 12 Proposed equation for barium sulphate precipitation deep within limestone\textsuperscript{66}

More recently Mattein\textsuperscript{69}, in the study of detrimental sulphation on mural and wall paintings has advocated the use of barium hydroxide in the complete conversion of gypsum to barium sulphate in a two step process. It is shown that due to the relatively low solubility of calcium sulphate dihydrate (0.015M) and barium sulphate (1.03 \times 10^{-5}M), direct conversion to barium sulphate with barium hydroxide solutions would only involve surface transformation of the crystals. Hence a pre-treatment step which converts the gypsum into a soluble sulphate before reacting with barium hydroxide is recommended, Figure 13.

\[
\text{CaSO}_4\cdot\text{2H}_2\text{O} + (\text{NH}_4)_2\text{CO}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3 + \text{2H}_2\text{O}
\]

Figure 13: Proposed reaction mechanism for gypsum conversion into barium carbonate\textsuperscript{70}
The direct conversion of gypsum on marble has also been investigated by Skoulidikis and Beloyannis\textsuperscript{71,72}, where the gypsum is converted back to calcium carbonate rather than barium carbonate. One of the described methods repeatedly saturates the marble with potassium carbonate solutions. Although not discussed it must be assumed that the by-product from the reaction is potassium sulphate, and generally any method producing a substantial concentration of additional salts is regarded as unacceptable.

The use of barium solutions on a large scale has not occurred and the use today is sporadic\textsuperscript{13} and often not reported in the literature.

2.2.1.2 Alkali silicates

Introduced mainly for the consolidation of sandstone and limestone, the intention was the formation of silica or insoluble silicates deposited into the pore structure of the stone, which would be less reactive to atmospheric agents. However, the reaction mechanism often resulted in the formation of soluble salts as by-products, which as mentioned before is undesirable for the conservation of any stone. The use of alkali silicates was first reported in 1861, by Ransome\textsuperscript{61}, where sodium silicate and calcium chloride were applied successively to the stone thus precipitating insoluble calcium silicate with the undesirable by-product of sodium chloride. In Hemingway’s patent application in 1910, he advocates the reaction between sodium or potassium silicate and acids such as hydrochloric, arsenic and carbonic acids to precipitate silica. Obviously, not an ideal mix of chemicals for marble surfaces and again salts as by-products are also formed. Apart from the problems associated with soluble salts, many silicates were found to deposit only at the surface and generally no significant consolidation was observed in situ. During the early 1970s Wihr and Steenken\textsuperscript{73}, again postulated the use of silicates for conservation on many stones including marble, using soluble sodium silicates and “calcium ion solutions”. They observed consolidation, but although noting that significant salt efflorescence occurred, they seemed unaware that this would most probably be due to the by-product from the reaction of the two components.
report by Riederer, a couple of years later reports the decline in use due to lack of deep penetration, surface flaking and salt efflorescence

2.2.1.3 Lime Methods

Lime methods for consolidation of weathered marble and limestone have been used for many centuries, and derive from the use of mortars that pre-date the Roman Empire. The basic concept being that lime (calcium hydroxide) is applied in solution where subsequent evaporation of water results in the deposition of solid calcium hydroxide within the pores, which react with CO$_2$ in the air to give calcium carbonate that acts to bind to the original material. As a technique nothing could be better than using clear limewater solutions as no by-products other than water result from the conversion of calcium hydroxide. However the limitation of the method is the low solubility of calcium hydroxide, and the long carbonation time required to convert solid calcium hydroxide in a porous structure to calcium carbonate. This has resulted in conflicting opinions on the success of the use of lime methods.

Lime methods have been extensively tested in England on limestone monuments as well as in Greece and Germany on marble monuments. Typically methods involve the use of pastes, poultices and clear limewater solutions. Professor Baker, developed the “lime technique” that has been tested throughout the UK on limestone monuments. This is effectively a four-stage conservation technique. Firstly the surface is cleaned with a hot lime poultice of freshly slaked lime, (Ca(OH)$_2$), applied to a thickness of 2-3 cm and kept moist over a three week period by applying water daily and keeping the poultice covered with sacking and plastic sheeting. The poultice is then carefully removed and any remaining dirt dislodged by softening with water and brushing particles away. The limestone is then consolidated by “flooding the surface with limewater over a period of a few days”, where they report the need for approximately forty applications. Excess limewater on the surface is removed between applications. Next, surface repairs are made using lime mortars, (no hydraulic mortars are used), these consist of lime and aggregates,
where the aggregates are either sand or stone dust (for marble restoration crushed marble is used). The proportions of the mortar constituents are dependent on function and are summarised in Table 3.

<table>
<thead>
<tr>
<th>Mortar Function</th>
<th>Lime</th>
<th>Aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repair mortar</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Adhesive mortar for re-fixing loose flakes</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Grouting mortar</td>
<td>1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3: Mortar proportions of constituents for 'lime method'

In the adhesive and grouting mortar up to 10% crushed ceramic is required as a pozzolanic additive. Where the term pozzolanic refers to the whole class of minerals that when mixed with lime and sand gives superior hardness that resists the action of water, known since ancient Greek and Roman times, texts by Vitruvius among others details their properties.

Once the surface repairs have been completed the surface is then protected with a thin ‘shelter coat’, more traditionally referred to as a limewash. Since this predominantly consists of lime and fine aggregates of sand and stone dust bound with a little casein it is still susceptible to the action of pollutants and is protective only in that it acts as a sacrificial layer delaying the pollutant effect on the stone underneath.

Variations from these methods have been tried periodically over many years and conflicting reports on the success of calcium hydroxide as a consolidant exist. On the work carried out using the lime method, Price, was unable under laboratory conditions to conclusively prove the consolidation effect that had visibly occurred on the sculptures at Wells Cathedral. It was later found that the calcium hydroxide had deposited in the outer couple of millimetres of the limestone. However, Moncrieff and Hempel, describe methods of
application of calcium hydroxide solutions to Carrara marble and other sculptural stone and suggest that an increase in hardness was observed throughout\(^8\), which may suggest that a difference in petrology between marble and limestone may affect the action of the limewater. In Germany limewater has been used extensively even though it is accepted that the consolidation effect is ‘short-lived’. The use is regarded as a maintenance measure to be repeated at regular intervals\(^2\).

Over the last twenty years conservation of the Acropolis monuments has also used lime-based methods, as a saturated solution, or in suspension as lime-milk or paste as lime putty\(^2\). Procedures for the surface consolidation are dependent on the actual conservation required. After cleaning of loose or detached larger fragments they are reattached with white Portland cement, often reinforced with titanium dowels. Smaller flakes are reattached using mortars based on mixtures of cements, solid lime, and calcium carbonate (6%)\(^3\). Grouting and shallow cracks are filled with cement and lime mixtures and where the surface is very friable mixtures of lime suspensions and calcium carbonate (6%) are applied to the surface very much like a sheltercoat. Work by Skoulikidis et al. on these lime methods, have proposed, like Dennstadt\(^6\), the use of carbon dioxide atmospheres at temperatures no greater than 35°C to precipitate small crystals. The added calcium carbonate is suggested to act as an autocatalysis for the carbonation of solid lime to calcium carbonate\(^4\). When two pieces of marble are joined using a paste of the above constituents under a CO\(_2\) environment for a few weeks adhesion between the two is observed.

The sole use of limewater as a consolidant has therefore produced conflicting opinions on the effectiveness of this method, and it is certainly true that only with numerous applications will sufficient material be deposited to significantly reduce the overall porosity of the stone\(^5\). It is still unknown how the calcium hydroxide deposits within the pore structure and what the effect of localised conversion to calcium carbonate has on the overall consolidation. Generally, however, lime methods consist of many steps where the use of calcium
hydroxide is most effective when used in mortar mixes as an adhesive, grout or filler.

More recently other ways of re-precipitating calcite back into the fabric of calcareous stones has been investigated and Tiano\textsuperscript{86}, suggests the use of organic matrix macromolecules extracted from \textit{Mytilus californianus} shells. The extracted glycoprotein is believed to be responsible for the formation of the calcareous shells of molluscs, however a calcium ion source is still required for precipitation of calcite. Work is still continuing in this area to find a better calcium ion source and the potential use of more readily available proteins.

2.2.2 Organic / Polymeric Based Consolidants

The use of organic polymer based consolidants, developed during the 1960s from the array of polymers that became commercially available, as Price\textsuperscript{59}, highlights in his review,

\begin{quote}
\textit{"Materials have been selected more on the grounds of availability than of any predetermined qualities."}
\end{quote}

Primarily these consolidants are based on the use of monomers, which are polymerised in situ or polymeric resins applied in a suitable carrying solvent. Many were developed for the use on sandstone and limestone and have been tried on many other stones such as marble with little regard for compatibility. Again Price\textsuperscript{59} points out that little is known of the actual science behind most consolidants; however, it should be considered that cement, that has been in existence since Roman times, is still the basis of extensive fundamental research.

The most prolific use of organic consolidants, from the many that have been tried, can be classified under three main headings:
1. Acrylic Polymers

2. Epoxy Resins

3. Alkoxy silanes

2.2.2.1 Acrylic Polymers

The acrylic systems generally used are derived from the acrylic acid monomer where the repeat unit is given in Figure 14.

Based on concrete consolidation, initial research suggested the use of acrylic monomers that would be polymerised in situ. Methyl methacrylate (MMA) and butyl methacrylate were two acrylic monomers initially studied. The former is slightly cheaper and penetrates faster than the latter, which is less volatile and more flexible. Polymerisation however requires either:

1. Heating at greater than 80°C with an initiator such as benzoyl peroxide or AIBN

2. Initiating by gamma radiation

3. At ambient temperature using promoters and initiators, where the promoter converts the initiator into free radicals hence inducing polymerisation
The susceptibility of some of the initiators to oxygen required that the impregnation of the stone be carried out under a vacuum. Heating large masses of stone and using evacuated methods is however impracticable, and the methods only found use for the conservation of small museum objects. Additionally during the polymerisation process the polymers shrink by up to 20%. Combined with their high glass transition temperatures, they are regarded as rigid and brittle polymers that generally are unsuitable for stone consolidation. Acrylic monomers are still used occasionally and Sinner\textsuperscript{88} advocates the complete impregnation of marble with polymethylmethacrylate, a consolidation technique in use from 1974 that completely fills the pore void space. Little regard is given to the difference in thermal expansion coefficients between the marble and acrylic resin approximately $7 \times 10^{-6}$ per °C and between 70 -- 80 $\times 10^{-6}$ per °C respectively\textsuperscript{12}. Hence deteriorated marble completely filled with an acrylic resin may have large internal forces.

In an attempt to circumvent the problems of polymerisation in situ, the application of acrylic resins dissolved in solvents was attempted. To ensure initial penetration, the viscosity of the solution cannot be too high and typically no greater than 10% weight:volume of the polymer in solution can be used\textsuperscript{89}. Laurenzi et al, compare the treatment of Carrara marble using methyl methacrylate applied as a monomer and polymethylmethacrylate applied in solution\textsuperscript{90}. Although it was observed that the monomer-based system was the better consolidant the induced colour alteration was greater with the monomer system than the polymer consolidant.

The earliest problem observed with polymer-solvent consolidants was the lack of deep penetration due to the volatility of the solvent, (typically trichloroethylene). On evaporation the solvent acted to draw the polymer back to the surface leading to the formation of surface crusts, enhanced erosion and colour alterations\textsuperscript{74,91}. Other less volatile carrying solvents have been used to attain greater penetration e.g acetone, isobutyl methyl ketone, dioxane and 2-ethoxyethanol\textsuperscript{92}. The most prominent acrylic polymer used for marble...
consolidation is Paraloid B72, reported to be a copolymer of ethylmethacrylate
and methylacrylate with a molar ratio of 70:30. Originally used as an
adhesive for reattachment of flakes, dilution of the acrylic resin has seen its use
grow as a marble consolidant. The use on marble appears to be more
successful than the use on limestone, where on limestone it is suggested to
show only partial migration, and the use of monomers polymerised in situ or
low molecular weight PMMA is recommended. Although it is generally
accepted that the depth of penetration of polymers applied in a solvent is not as
great as the use of monomers, paraloid B72 is still one of the most widely used
marble consolidants. In use since the late 1960s for consolidation of external
sculpture, notable case studies include marbles such as on the façade of St
Peters in the Vatican, to those located within the UK.

PMMA is regarded as stable to degradation by heat and oxygen and ultraviolet
ageing, as opposed to the lower Tg methacrylate polymers that tend to have a
tendency to cross link under ultraviolet exposure whereas all acrylates cross
link on ultraviolet exposure. Paraloid B72 is regarded as more stable to the
action of heat and ultraviolet radiation, not becoming insoluble and thus
allowing for removal where used as an adhesive. Some reports have suggested
that the acrylics do age and yellowing on the Taj Mahal has been partially
attributed to acrylic resins at the surface.

2.2.2.2 Epoxy Resins

Charles Selwitz in his review of epoxy resins for stone conservation covers in
great detail both the failures and success of the system offering a scientific
explanation, that is notably lacking for other consolidants.

Epoxy resins have been widely used as adhesives to repair detached fragments
but for the stabilisation of friable stone they are regarded with caution. They
have notoriety for being viscous on application, brittle on hardening and
discolour with ageing. The reluctance to use epoxy resins in conservation
propagated from the initial research during the 1960s. Commercial resins obtained were used according to set guidelines and were too viscous to give any penetration. The resin cured to form crusts that looked ready to spall from the surface and that caused discoloration.

Epoxy consolidants and adhesives are two component systems, an epoxy resin and a curing agent where mixing the two causes the conversion into a hard cross-linked polymer. The epoxy resin contains a strained three membered epoxide ring functionality and the curing agent is normally based on an aliphatic amine compound. The amine reacts through the hydrogen to open the epoxide ring and form a secondary alcohol, Figure 15. Their properties include high strength and good adhesion to many substrates, with only 5% shrinkage on curing and good chemical resistance to alkali, acid, water and salt solutions.

Figure 15: Epoxy-amine cross linking reaction

Historically the typical epoxy resins used in consolidation are derived from bisphenol A diglycidylether, prepared by the reaction between diphenylolpropane (bisphenol A) and epichlorohydrin, Figure 16.
Figure 16: Epoxy resin formation for use in stone consolidation

It is possible for the phenol to polymerise with the epoxide group and often the commercial resins, before polymerisation with the curing agent, contain linear polymers with up to twenty repeat units. The viscosity of epoxy resins based on the bisphenol A diglycidyl ether range from 1000 - 16000 cP at 25°C\textsuperscript{100} compared to water which has a viscosity of 1 cP.

The other main group of epoxy resins developed for stone consolidation is based on aliphatic epoxy resins and a selection are shown in Table 4. They are much less viscous than the bisphenol A derivatives, with the viscosity ranging from 3-500 cP\textsuperscript{100} and generally are more stable to colour alteration due to the lack of aromatic functionality.
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<table>
<thead>
<tr>
<th>NAME</th>
<th>STRUCTURE</th>
<th>VISCOSITY cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butyl glycidyl ether</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Poly(propylene glycol)</td>
<td></td>
<td>30-100</td>
</tr>
<tr>
<td>di glycidyl ether</td>
<td></td>
<td>~ 20</td>
</tr>
<tr>
<td>Alkyl diglycidyl ether</td>
<td></td>
<td>~ 30</td>
</tr>
<tr>
<td>Resorcinol diglycidyl ether</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Low viscosity epoxy resins

There is also a large variety in the number of amine curing agents available for stone consolidation and Table 5, gives just a few.

<table>
<thead>
<tr>
<th>NAME</th>
<th>STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylenetriamine</td>
<td>H₂N-(CH₂)₂-NH-(CH₂)₂-NH₂</td>
</tr>
<tr>
<td>Triethylenetetramine</td>
<td>H₂N-(CH₂-CH₂-NH)₂-CH₂-CH₂-NH₂</td>
</tr>
<tr>
<td>Tris(dimethylaminomethyl)phenol</td>
<td>(CH₃)₂NCH₂CH₂N(CH₃)₂</td>
</tr>
<tr>
<td>Menthane diamine</td>
<td>CH₃-C-CH₂-C-CH₃</td>
</tr>
</tbody>
</table>

Table 5: Typical amine curing agents

The properties of the amines influence both the rate of curing, which is important for increasing the depth of penetration, and secondly can reduce the susceptibility of the cured resin to colour alterations. The traditionally used low viscosity amines such as diethylenetriamine and triethylenetetramine cure
quickly at ambient temperatures but are toxic and led to the discoloration of the cured polymer. Their use has been minimised and less volatile derivatives such as mixes of epoxy resin and excess polyamines as well as amidoamines are more commonly recommended. Although cure times are much slower, many give products that are stable to oxidation and colour alterations. Many of the amines are sensitive to the action of carbon dioxide and the primary aliphatic and cycloaliphatic amines react at room temperature in humid environments to give amine carbonate that produces white efflorescence at the stone surface and insufficient curing of the epoxy resin.

The discoloration of cured epoxy resins on exposure to oxygen and sunlight has been the subject of much research, since it is primarily this factor that has deterred use\textsuperscript{101,102}. The presence of amine groups and aromatic functionality yields chromophoric structures that tend to give rise to yellow discoloration. Although it is suggested that aliphatic epoxy resins rather than the amine-based derivatives are more light fast it has been shown that the composition of the amine hardener is more critical. The light stability of the aminopolyethyleneamine derivatives is worst and increased stability can be achieved by the inclusion of oxygen containing functionality.

The early work during the late 1960s and early 1970s to overcome the problem of poor penetration into marble using non-solvent systems lead Hempel and Moncreiff to investigate the use of epoxy resins at high temperatures that would encase any soluble salts\textsuperscript{81,103}. Using commercially available Marasett resins, based on the conventional bisphenol A diglycidyl ether and aromatic amines, mixed with dibutyl phthalate to reduce the viscosity, they worked at 72°C. Protective sheeting wrapped around the marble sculpture after application was used to minimise the observed oxidation of the resin at this temperature (presented as white bloom at the surface). Although reporting promising results, working conditions were intolerable, dangerous and toxicologically harmful and little progress has been made with this method. Munnikendam advocated the use of low viscosity formulations diluted with
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tetraethoxy silane to give a viscosity of 2 cP, however poor penetration was still observed and the butanediol diglycidyl ether used was found to discolour. Selwitz reports in his review that more recent research has shown that the low viscosity diepoxides such as Munnikendams recommendation show a tendency to absorb water leading to swelling and disruption of the stone/consolidant interface. Gauri, one of the main researchers in epoxy resin consolidants observed that marble coated with some aliphatic epoxy resins showed increased reactivity towards the action of SO$_2$(g), being five times more susceptible to deterioration as compared to untreated marble. Unlike the aromatic epoxy resins which are low surface energy materials the high proportion of oxygen functionality in the low viscosity resins results in a more hydrophilic coating that acts to hold the water and hence sulphuric acid against the calcite surface.

The use of non-solvent based systems generally gave shallow penetration into stone and the use of solvents for the reduction of viscosity is more commonly practised. A solvent will effect the cure rate and the interaction between the consolidant and stone surface. Alcohols are found to accelerate the cure rate whilst aprotic solvents such as aromatic hydrocarbons act as inert diluents and acetone and methyl ethyl ketone retard the cure rate.

The development of the use of epoxy resins in solvents have moved in two directions.

1. To use the traditional epoxy resins based on the aromatic system, bisphenol A diglycidyl ether (such as is used in Araldite), and basic polyamine hardeners. Research has focussed on avoiding the associated colour and impregnation problems by careful consideration of application techniques.

2. To develop aliphatic epoxy resins which have a much lower viscosity and are less likely to discolour on ageing.

The use of the aromatic resins, even with all the problems associated with them, has been predominantly in America on marble monuments. The low cost, high mechanical strength and fast cure times outweighs any potential
discoloration. Gauri has been the main advocate for aromatic epoxy derivatives and recommends treatment by spraying or soaking the surface with acetone diluted epoxy resins and polyamine curing agents (10-30%)\textsuperscript{104,105,106}. To avoid surface discoloration it is suggested that the surface be wiped with acetone or abrasively cleaned. Comparison to other consolidants such as methyltrimethoxysilane, acrylic resins and acrylic and silane mixes resulted in epoxy resins increasing the strength of the stone more than the other methods\textsuperscript{107}. However, the idea of abrasively removing the resin from the surface to prevent discoloration is generally regarded as unacceptable for the conservation of sculpture.

Marinelli\textsuperscript{108}, investigated the use of low viscosity aliphatic epoxy resins as an alternative to the bisphenol A derivatives suggesting the use of pentaerythritol tetraglycidyl ether with either a cycloaliphatic amine or an aromatic amine, the use of the latter gave better chemical resistance at the expense of UV degradation. The systems were diluted with acetone-water mix. During the 1980s the use of cycloaliphatic epoxy monomers were tested for Proconessian marble consolidation\textsuperscript{109}. Mixed in a 5:1 ratio with an aliphatic polyamine, as a 25% by volume solution in an isopropanol-toluene solvent mix, colour stability and improvement in compressive strength were studied. To ensure that no ammonium carbonate would form, an induction period of 2 - 8 hours is employed after mixing and before application, thus giving a less active curing agent, full polymerisation takes over 48 hours. There was no change in appearance of the stone and the compressive strength for decayed marly limestone increased from 860 kg/cm\textsuperscript{2} to 1500 kg/cm\textsuperscript{2} after treatment.

The use of epoxy resins therefore requires careful control and predetermination of long term stability if it is to be used for the conservation of sculpture. Too viscous to be used without a carrying solvent, deep impregnation is only achieved by methods such as spraying using acetone to aid capillary uptake or complete immersion. Problems of curing agent susceptibility to carbon dioxide should be addressed as well as the UV instability, although Selwitz\textsuperscript{100}
comments that field trials show that often the discoloration disappears after a period of time due to the complete oxidation of the surface resin. Also issues such as pore filling should be avoided as again the thermal expansion coefficient of epoxy resins is $60 \times 10^{-6}$ per °C over eight times greater than marble. Provided these issues can be addressed then the use of epoxy resins offers high mechanical strength and often increased resistance to acidic gas attack and no by-products. Although commercial resins often contain impurities that have been suggested to also cause discoloration of the surface.

2.2.2.3 Alkoxysilanes

Alkoxysilanes, specifically designed for sandstone, are the most prolifically used general stone consolidant of the last thirty years, in particular are those derived from the monomers methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS), Figure 17

![Methyltrimethoxysilane and Tetraethoxysilane](image_url)

**Figure 17:** Two major alkoxysilane monomers used in stone consolidation

Alkoxysilanes react with water, often in the presence of a catalyst, to form a silica gel, (a gel because of water hydrogen bonding to the hydroxy groups present after hydrolysis), that coats the pores and eventually hardens via
condensation polymerisation. The general reaction mechanism begins with the hydrolysis of the monomer brought about by the presence of water, hence the material must first be pre-dried to avoid gel formation at the near surface and hence the water must be added at a later stage after impregnation. Catalysed condensation polymerisation then occurs with the loss of water, where curing is dependent on the loss of alcohol by evaporation that may take many days. The basic reaction mechanism is shown in Figure 18

\[ 2 \text{R-Si-OR} + \text{H}_2\text{O} \rightarrow \text{R-Si-OH} + \text{HO-Si-R} + 2\text{ROH} \]

\[ \text{S-Si-O-Si-R} + \text{H}_2\text{O} \]

Figure 18: Schematic reaction of condensation polymerisation of alkoxy silanes

The polymerised product is chemically similar to the natural cementing materials found in sedimentary rocks such as sandstone. The presence of Si-OH groups on the sandstone surface allows for chemical bonding to the consolidant, forming a silica (tetrathoxysilane monomer) or alkyl polysiloxane (methyl trimethoxysilane monomer) lattice. The latter with the alkyl group effectively increases the hydrophobicity of the stone with reduction to overall consolidation effect.

Designed for use on sandstone, the alkoxy silanes have been used on both limestone and marble, with little regard for the considerable differences in the
properties of both materials. These differences have led manufacturers to list alkoxysilanes as sandstone consolidants only\textsuperscript{85} however, despite the commercial reluctance to endorse alkoxysilanes for calcareous stones, conservators have investigated their effects. Hempel and Moncrieff during the early 1970s reported the results from a study of saccharoidal carrara marble\textsuperscript{111}. Impregnation using silicone monomers to an optimum depth of 30mm were found to consolidate the material even after 6 years exposure to London’s atmospheric environment. The application to the marble sculpture, included drying followed by adsorption of 2-ethoxyethanol and then brushing the surface repeatedly with a mixture of methyl trimethoxysilane (45\%), 2-ethoxyethanol (50\%) and water (5\%). Once saturated, the sculpture needed to be left for a period of six weeks to allow polymerisation. In comparing the effect of tetraethoxysilane, triethoxysilane and methyltrimethoxysilane for the consolidation of powdered marble only the latter was found to be successful. How the silanes consolidate the marble is not considered but it is possible that the surface of the marble contains some hydroxide groups and consolidation occurs at these points.

Subsequent to the above work, the 1970s saw the emergence of “Brethane” used for the conservation of limestone at Wells Cathedral\textsuperscript{112}, the use of mixtures methyltrimethoxysilane and the acrylic resin B72 for the conservation of marble and limestone (for limestone this is commonly referred to as the ‘Bologna cocktail’)\textsuperscript{107}. Mixing of these two consolidants in trichloroethane apparently gave superior characteristics. The alkoxysilane reduced the viscosity of the acrylic resin allowing for greater depth of penetration, whilst also reducing the extent of reaction to acidic gases. However Wheeler \textit{et al}\textsuperscript{107}, have reported that the presence of the alkoxysilane has no effect on the consolidation of stone. Verges-Belmin \textit{et al}\textsuperscript{113}, studied seven consolidation treatments for decayed Carrara marble comparing acrylic resins to alkoxysilanes and found the latter to produce the best results.
Alkoxysilanes are resistant to the action of heat and moisture, but like most of the polymer based consolidants they are susceptible to the action of ultraviolet light and the resins eventually break down to a white powder. Although a large penetration depth can be achieved most of the polymerisation methods are expensive requiring a large quantity of materials to secure a deep penetration. They have also been shown to be susceptible to the action of enzymatic and catalytic degradation and have differing thermal expansions compared to the stone. Also it is reported that they can cause the stone to become blocked so not allowing the escape of water vapour and soluble salts. As such they do provide the best solution as yet to the problem of consolidation of the friable stone and protection from water absorption and have been used primarily on many limestone buildings and monuments such as St Paul’s Cathedral, Bolsover castle, and Oxford colleges.

2.2.3 Protective Coatings

Initially it was hoped that a single consolidant would also act as a protective agent against further weathering, for example the work of Gauri on epoxy resins. However, it is generally accepted that an additional component is required to afford protection from acidic gases and salt cycles, although most have been developed from consolidating mechanisms. Since water is the precursor in most of the weathering mechanisms surface coatings have been primarily focussed on water repellence.

Historically surface protection was afforded by the use of hydrophobic coatings of natural materials such as linseed oil, animal fats (fatty stearates) and waxes. Waxes are the oldest known preservative, described by Vitruvius for impregnating stone. They were applied by rubbing solid wax into a warmed surface or if possible immersing the whole artefact in molten wax. More recently paraffin wax has been used, which not only made the surface hydrophobic but also acted as a consolidant, presumably because of complete pore filling. However, wax based systems often lead to discoloration,
they soften an relatively low temperatures adhering particulates to the surface and trapped salts eventually penetrate to the surface often causing loss of material\textsuperscript{85,116}. Linseed oil tends to change the appearance of the stone and stearates have been suggested to liberate acids on decomposition\textsuperscript{117}.

More modern water repellants are derived from the alkoxy silane consolidants where silicones coat the surface with the polar part orientated towards the stone surface and the aliphatic region extends away from the surface to provide a hydrophobic barrier, Figure 19.

![Hydrophobic region](image)

\textbf{Figure 19: Silicone water repellent}

Gauri and Madiraju\textsuperscript{118}, studied the effect of silicone resins for the protection of marble to acidic sulphur dioxide attack and found that several different silicones actually increased weathering. This may indicate that alkoxy silane based derivatives do not bind to marble in the same way as sandstones, presumably due to less hydroxy groups on the surface. As a result the polymer chain may extend away from the surface, where the polar functionality creates channels, that hold the water close to the surface allowing for sulphur dioxide attack, Figure 20.
From this research it was found that a fluorinated acrylic resin appeared to almost eliminate the formation of calcium sulphate dihydrate and the development of fluorinated acrylic resins for stone protection is reported\textsuperscript{119}. Matteini has suggested the conversion of the marble surface to calcium oxalate (scialbatura)\textsuperscript{120}. He proposed the use of ammonium oxalate to produce a layer approximately 10 \( \mu \)m thick that acts as a barrier to the action of acidic gases whilst not making the marble surface hydrophobic so that water vapour and salts may still permeate through the stone. Trials are still continuing with this method, although a preliminary study by Cezar\textsuperscript{121} on limestone showed that reaction in a saturated sulphuric acid environment continued, however it could not be ascertained whether the calcium oxalate was distributed evenly across the surface.

Finally in Prices review\textsuperscript{59} he reports the work of Kozlowski on the use of sols of colloidal silica for the protection of calcareous stones by deposition within the outer pores which impedes the flow of water, such a method is unlikely however to inhibit acidic gas attack on marble.
Generally protective coatings have met with limited success and to date not one compound has become used as standard for the protection of marble sculpture.

2.3 Summary

The conservation of sculpture usually entails cleaning and depending on the extent of weathering some form of consolidation and protection. In terms of the consolidation, numerous methods exist, which all are found to have varying success. No method is perfect and all the discussed procedures usually have one or more limitations where these can include low solubility, poor penetration, UV instability and thermal expansion differences. Research continues into these areas to try and minimise limitations and maximise consolidation effect.
Chapter 3 SURFACE CHARACTERISATION TECHNIQUES

The objective of the research has been to develop a consolidation procedure for the conservation of the Ince Blundell collection of marble sculptures. In order to characterise, develop, and test samples and potential procedures, four main techniques have been used.

1. **Diffuse reflectance infrared Fourier transform spectroscopy** (DRIFT)
2. **X-ray photoelectron spectroscopy** (XPS)
3. **Scanning electron microscopy** (SEM)
4. **Mercury porosimetry**

The first two techniques allow quantitative determination of the surface chemistry, whilst the latter two techniques allow physical characterisation of surface and bulk properties of the marble. A brief theoretical description of each of these main techniques used is given in the following section, indicating why they have been selected and how their results are to be interpreted.

### 3.1 Fourier Transform Infrared Spectroscopy (FTIR)

#### 3.1.1 Basic Principles

FTIR spectroscopy is based on the principles of interferometry. An infrared source, which radiates light over a broad range of infrared wavelengths is split into two paths using an IR beam splitter. The IR radiation is then reflected from two mirrors back onto the beam splitter where the paths are recombined. One mirror is fixed and the other mirror moves. As the distance between the beam splitter and the moving mirror varies, a difference in phase between the two path lengths will lead to constructive and destructive interference for different wavelengths of light. The resulting interferogram is a combination of all the individual interference patterns for most wavelengths and is detected as
a function of mirror travel. The interferogram can be converted into an IR spectrum by the use of the complex mathematical operation known as Fourier transformation. The interferometric optical arrangement is known as the Michelson Interferometer and a schematic is given in Figure 21.

\[ \text{Michelson Interferometer} \]

\[ \text{FT Analysis} \]

Source of Radiation

Beam Splitter

Mirror

Moving Mirror

Displacement measured using a laser

Sample

Detector

Path Difference

Abs

IR Spectra

Wavenumber

Int

\[ \text{Figure 21: Schematic of the Michelson Interferometer used in FTIR apparatus.} \]

If the beam is directed onto a sample, which absorbs IR radiation, the interferogram is modified according to the wavelengths adsorbed. Hence the modified interferogram contains all the absorption information for the entire frequency range, known as the 'Fellgett' advantage. This allows for rapid acquisition of spectral data compared to dispersive instruments, and thus signal to noise can be improved by increasing the number of scans, typically a minimum of 150 scans per sample are taken. Thus for highly absorbing materials such as marble and weathering products, small quantities of material can be analysed giving a good signal to noise ratio. The Fourier transformed interferogram results in the equivalent of a single beam spectrum of intensity
versus wavenumber. The spectrum also incorporates source and beam splitter characteristics and any absorbances due to water vapour and carbon dioxide. To minimise these contributions a background spectrum is recorded without the sample and subsequent spectra are ratioed to the background spectrum. Finally the other main advantage of FTIR spectroscopy over traditional dispersive techniques is the high throughput of radiation (Jacquinot advantage) since there is no need for narrow slits.

3.1.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)

FTIR reflectance techniques are used primarily for the study of powders, rough surfaces, and coatings on such solids\textsuperscript{122,123}, and for the study of the marble surfaces and protective coatings reflectance techniques can be applied.

IR radiation will scatter and reflect from any interface where there is a difference in the refractive indices between the two contacting phases i.e. air and the sample. As the radiation reflects from another phase it can penetrate the surface by the order of one wavelength. The reflected wave will contain characteristic structural and chemical information on the material being studied, if the material adsors within the mid infrared region, and summed with the scattered radiation constitutes the diffusely reflected IR.

In the case of diffuse reflectance the rough surfaces of powders transmit and reflect the radiation in random directions resulting in the widening of the originally narrow beam\textsuperscript{123}. Therefore the infrared radiation, diffusely reflected from a sample, is collected by an elliptical refocusing mirror before passing to the detector.
The reflected radiation can also contain contributions due to specular reflection. The specular component, is the energy reflected from the front surface of the powder only. For matt powders this should be minimal but any specular component measured will effect quantitative treatment of results accounting for diffusely reflected IR only. Reduction in the specular reflection can be achieved by:

1. By blocking the front surface-reflected energy directly at the sample with a metal blade. Therefore in order to reach the collection mirror the infrared radiation must penetrate into the powder and be diffusely scattered. Any energy reflected without penetration into the powder (i.e. specular reflectance) should be blocked by the metal blade.

2. Keeping particle size small. As the particle size of a highly absorbing material increases, the amount of radiation diffusely reflected is reduced because the radiation is adsorbed more before it can be scattered or reflected back from the sample. Hence if the particle size is large and concentrated specular reflection may dominate the spectrum.
3. To maximise the contribution from radiation that has penetrated the sample, the sample is diluted in a non-adsorbing but highly scattering matrix such as KBr.

3.1.2.1 Quantitative Treatment

A number of theories have been developed for the quantitative treatment of DRIFT spectra and they essentially fall into two groups: (i) Continuum Theory (ii) Statistical Theory. The statistical theory is based on the mathematical construction of an appropriate model, where the success of the theory depends on the closeness of the model to the real sample conditions\textsuperscript{125}. If the model correlates well to the real sample then it is possible to measure the fundamental properties of scattering (i.e. particle size, refractivity index, absorptivity, etc.). However the statistical theory is mathematically cumbersome and not readily used.

The most common theory encountered, is the continuum model where the absorption and scattering characteristics of the medium are accounted for by phenomenological constants. Such models are varying degrees of approximation of the equation of radiative transfer, with the most implemented and practical approximation being the Kubelka-Munk theory\textsuperscript{126}. The theory relates the sample concentration and diffusely reflected radiation much in the same manner as Beer's Law. In the model, the powder is considered to be a homogeneous material, where the scattering property and reflectivity are those of the powder as a whole rather than the sum of the individual optical properties. The reflectance, \( R \), is the total intensity of radiation emitted from the sample and detected. It is governed by two fluxes \( I_+ \) the radiation travelling into the bulk and \( I_- \) the radiation travelling towards the surface. The intensity of the radiation travelling into the bulk is decreased by scattering and absorption process, (both assumed to be proportional to the thickness of the medium), partially offset by the scattering from the radiation travelling in the other direction. The radiation travelling towards the surface is also determined by both scattering and absorbing coefficients denoted \( S \) and \( K \) respectively.
Hence \( R = \frac{I_0}{I_+} \). For an ‘infinitely thick’ layer, the Kubelka – Munk equation is written as:

\[
f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S}
\]

Equation 2: Kubelka – Munk equation.

Where \( R_\infty \) is the absolute reflectance of a layer so thick that an increase in thickness does not alter the reflectance. \( S \) is the scattering coefficient and \( K \) is the molar absorption coefficient and \( f(R_\infty) \) is the Kubelka – Munk function. No sample is perfectly diffuse reflecting and \( R_\infty \) is replaced by \( R'_\infty \), given by:

\[
R'_\infty = \frac{R'_\infty(\text{sample})}{R'_\infty(\text{standard})}
\]

Where \( R'_\infty(\text{sample}) \) represents the single-beam reflectance spectrum of the sample and \( R'_\infty(\text{standard}) \) is the single-beam reflectance spectrum of the non-absorbing background (KBr) that is highly scattering for all wavelengths (i.e. minimal contribution from \( K \)).

The theory therefore predicts a linear relationship between the molar absorption coefficient, \( K \), and the peak value of \( f(R_\infty) \) for each band providing \( S \) remains constant. For dilute composite samples in low absorbing matrices the absorption coefficient is given:

\[
K = 2.303 \sum_{i=1}^{N} a_i c_i
\]

Where \( a_i \) and \( c_i \) are the absorptivity and concentration of the \( i \)th component.

It is here that the theory can break down, for \( S \) is dependent on the absorption, particle size, shape, dispersion and concentration of sample as well as the size of the diluent particles\(^{127}\). Such dependency makes the Kubelka-Munk theory a limiting law for moderately absorbing species at controlled particle size. It is therefore important in the present study to keep to the same sample preparation
for each spectrum so as to minimise the scattering coefficients variable parameters. As it is difficult to keep all parameters constant it is thought to be better to ratio two peaks, either two carbonate peaks or a carbonate peak and surface species peak, which compensates for small inconsistencies in sample preparation.

An ideal concentration of sample to diluent has been determined to give an absorbance below 1, which is in the instrumental linear range. It has been shown for thin stearic acid coatings on a surface that simple ratios of peaks in either absorbance units or Kubelka-Munk format, increase linearly with extent of coating and hence either could be used experimentally. However since the Kubelka–Munk format is regarded as more rigorous all spectra quantitatively analysed have been converted to $f(R_{\infty})$.

For powdered samples and loose material it will be possible to characterise them using the technique outlined above. However for surfaces where no loose material can be removed it is still possible to qualitatively analyse the surface by using an abrasive silicon carbide disc. This technique has been found to give similar results to a sample that is ground and measured under the standard method above.

3.2 XPS

X-ray photoelectron spectroscopy (XPS) can be applied to a wide range of materials in the gas, liquid or solid phase to yield varied analytical data. For the purpose of this study it is the information from solid surfaces that is of importance. XPS can give information on the composition of simple surfaces and the modification of such surfaces in a controlled manner.

3.2.1 Basic Principles

The basic principle of XPS is that interaction of an X-ray photon with a sample in a vacuum leads to the ejection of a photoelectron from inner shells
Photoemission will therefore occur when the electrons in the material have binding energies less than that of the energy of the exciting X-rays (Al Kα 1486.6 eV). The resulting electron vacancy in the sample is filled by an electron from a higher level, which can lead to either X-ray fluorescence, or the radiationless de-excitation process of Auger emission, Figure 23. It is the determination of the outgoing electron that is the main principle in the technique of XPS.

![Figure 23: Schematic representation of the generation of photo and auger electrons](image)

The kinetic energy (KE) of the ejected photon is related to its binding energy (BE), which is characteristic of the element and the atomic level from which it emanated. This is given in the general equation for conducting materials:

\[
KE = h\nu - BE - \phi
\]

Equation 3: Kinetic energy of photoelectrons

Where the function \( \phi \) is the instrumental work function of the spectrometer. Since the photon energy of the X-rays (\( h\nu \)) and the work function (\( \phi \)) are known and the KE is determined experimentally, calculation of the binding
energy is simple. The KE is measured by an energy analyser, which captures the ejected photoelectron. For insulating samples, binding energies are normally measured relative to adventitious carbon at 284.6 eV. The binding energy of a core electron is characteristic of the element from which it is emitted, therefore experimental measurement of kinetic energy allows characterisation of elements present. Detection limits are dependent on the element and can range from 0.1-1 atomic %

3.2.2 Surface Specificity and Quantification

Although the impinging photon can penetrate the substrate to a depth in the order of microns only the photoelectrons from the outermost 1-5nm actually escape from the surface without energy loss. This is because electrons generated in the bulk of the material have a high probability of undergoing inelastic collisions with neighbouring electrons. The depth at which photoelectrons have a probability of 1/e of escaping without energy loss is known as the attenuation length \( \lambda \) (formerly inelastic mean free path). \( \lambda \), is material and kinetic energy dependent and can be calculated according to the equations presented by Seah and Dench\(^{130}\), Table 6.

<table>
<thead>
<tr>
<th>Electron Source</th>
<th>Attenuation Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>( \lambda_M = \frac{538}{E^2} + 0.41(aE)^{1/2} ) monolayers</td>
</tr>
<tr>
<td>Inorganic Compound</td>
<td>( \lambda_M = \frac{2170}{E^2} + 0.72(aE)^{1/2} ) monolayers</td>
</tr>
<tr>
<td>Organic Compound</td>
<td>( \lambda_M = \frac{49}{E^2} + 0.11E^{1/2} ) mgm(^{-1})</td>
</tr>
</tbody>
</table>

Table 6: Equations for the calculation of attenuation lengths

\( \lambda_m \), the attenuation in terms of monolayers is related to the attenuation length \( \lambda \) by.
\[ \lambda = \lambda_m \alpha \text{ nm} \]

**Equation 4: Attenuation Length**

Where \( \alpha \) is given by:

\[ \alpha^3 = \frac{A}{\rho n N} \times 10^{24} \]

**Equation 5: Monolayer thickness (nm) for determination of attenuation length**

\( A \), is the atomic or molecular weight, \( n \) is the number of atoms in the molecule, \( N \) is Avogadro’s constant and \( \rho \) is the bulk density in kg m\(^{-3}\).

Quantitative analysis can give information on the atomic surface composition and the surface chemistry of each atom. The latter can allow characterisation of overlayers on a bulk substrate where the thickness of such layers can be determined when sample geometry and attenuation length are addressed.

The surface composition in terms of percent atomic concentration, \%[atom], can be determined from a broad scan spectrum by measurement of the relative intensities of the photoemission peaks after removal of the background. The intensity of each spectral peak can be written in terms of the number of photoelectrons per second \((I)^{131}\):

\[ I = n \chi \sigma \gamma \lambda TD \]

**Equation 6: Number of photoelectrons per second**

Where \( n \), is the number of atoms of the element per unit volume. \( \chi \) is the X-ray flux. \( \sigma \), is the photoionisation cross section and \( \gamma \) is the angular asymmetry factor. \( \lambda \), is the attenuation length. \( T \) is the transmission efficiency of the energy analyser and \( D \) is the detector efficiency.

\( \chi \sigma \gamma \lambda TD \) is assigned as the relative sensitivity factor (RSF) and can be either calculated using semi-empirical equations or derived experimentally by recording spectra of standard materials of known concentration. The percent
atomic composition can therefore be determined from rearrangement of Equation 6:

\[
\text{\%[atom]} = \frac{n_A}{\sum n_i} \times 100 = \frac{I_A/(RSF)_A}{\sum I_i/(RSF)_i} \times 100
\]

Equation 7: Percent atomic composition

Information on the surface chemistry can be obtained from a narrow scan spectrum, which is designed to give maximum energy resolution. The binding energy of a core level electron depends principally on the charge on the nucleus, however they are also slightly affected by bonding due to the valence electrons i.e. the change in oxidation state, and the electronegativity of neighbouring atoms. Thus the chemical environment surrounding the atom will affect the binding energies of individual atoms, known as ‘chemical shift’, where this shift is normally less than 10 eV. The chemical shift can allow the characterisation of different chemical species that contain the same elements. For the protective coatings on marble, the carbon photoelectron due to the carbonate can be differentiated from the carbon photoelectron due to an organic overlayer.

It is possible to measure the intensities of these peaks by using peak fitting programs such as Kwok V.4.1. The difference in binding energies may be less than 1 eV and when this is the case it is often necessary to further enhance the narrow scan spectra by deconvolution prior to peak fitting. This will remove factors such as the broadening due to the X-ray line shape. Mathematical manipulation of the peak intensities can allow for the calculation of depths of overlayers assuming the adsorbed layer is uniform and spherical in shape, and this is discussed further in the Part 3.
3.3 Scanning Electron Microscopy

SEM is useful in the observation of the surface topography of a sample and when used in conjunction with energy dispersive analysis of X-rays (EDAX) can give information on the elements present. This makes this an ideal tool for the characterisation of marble surfaces both before and after consolidation. Goodhew and Humphreys\textsuperscript{132}, provide an excellent review of electron microscopy and a brief outline of the fundamentals is given here.

The principle of SEM is that the interaction of primary electrons with a specimen causes their energy to be dissipated. This results in the majority of the energy being eventually lost as heat within the sample and approximately 5% escaping the surface either as backscattered electrons, secondary electrons or X-rays. Backscattered and secondary electrons are primarily used to generate the surface image whereas the X-rays, characteristic of individual elements, are used for chemical analysis. The region into which the electrons penetrate is known as the interaction volume, X-rays which are not easily absorbed will almost all escape from the surface with a sampling volume of the same order of magnitude as the interaction volume. Electrons will not be backscattered once they have penetrated more than 5nm and hence the backscattered electrons originate from a much smaller sampling volume with a sample diameter of \( \sim 0.1\mu m \). Although secondary electrons are produced by both primary electrons entering the specimen and by escaping backscattered electrons, the former are more numerous and hence secondary electrons are generally produced from a region not much larger than the diameter of the incident beam. The resolution of the SEM is related to the sampling volume and secondary electrons tend to give a better spatial resolution The interaction of the primary beam of electrons with a sample is summarised schematically in Figure 24.
The beam of electrons is normally produced by thermionic emission giving a stream of electrons which are accelerated to an energy of between 2keV and 40keV. A series of condenser lenses are used to focus the electron beam producing a diameter of between 2-10nm at the surface. The fine beam of electrons is scanned across the specimen by scan coils, while a detector counts the number of low energy secondary electrons emitted from each point on the surface. An amplified current from the detector controls the brightness of the spot of a cathode ray tube, which is simultaneously scanned across a monitor screen. For a good image it is usually necessary to have an electrically conducting surface. This is because on a non-conducting sample the number of secondary and backscattered electrons will accumulate on the surface and will form a negative charge repelling the incoming electron beam. The deviation of this beam causes a distortion of the image. Hence for non-conducting materials such as marble, the samples are sputter coated with a thin layer of gold, so
eliminating surface charging. This means that for SEM analysis of marble the sample analysed after running other analytical techniques.

3.4 Mercury Porosimetry

3.4.1 Basic Principles

Mercury intrusion porosimetry is based on the principle that a non-wetting liquid will only intrude capillaries under pressure. This phenomena is described by the Laplace equation\(^{133}\):

\[
P = \frac{-2\gamma \cos \theta}{a}
\]

_Equation 8: Laplace Equation_

Where \(P\) is the applied pressure under vacuum, \(a\) is the capillary radius, \(\theta\) is the contact angle of mercury, typically greater than 130°, and \(\gamma\) is the surface tension of mercury. Therefore as the diameter of the capillary decreases the pressure required to force mercury into the void increases.

The equation assumes cylindrical geometry where the porous material is considered to contain an array of capillaries. These can be interconnected and the errors are minimal provided all pores are equally accessible to the exterior reservoir of mercury. Generally pores are rarely cylindrical and the use of the Laplace equation therefore represents a model of the pore distribution, and is the accepted method for treating what would otherwise be a complex problem.

Deviations from the Laplace equation can be observed from the study of mercury intrusion and mercury extrusion experiments, where hysteresis is normally observed. Two main explanation are generally given:

1. Structural deviation from cylindrical geometry (the ‘ink-bottle’ effect) If a pore is accessed through a smaller pore diameter, it can only be filled once
the pressure required to fill the smaller diameter is attained\textsuperscript{134}. Therefore the intrusion data is biased toward smaller pores and conversely the extrusion curve is biased towards larger pores.

2. A pore potential exists. During initial intrusion mercury is not subjected to pore wall interaction but that on extrusion a pore wall interaction does occur. This is believed to cause a shift in contact angle between intrusion and extrusion\textsuperscript{135}.

Generally mercury porosimetry allows rapid characterisation of a very wide range of pore sizes (0.005 – 200 μm) where the macropore size (> 0.5 μm) cannot be reliably measured by other techniques such as gas adsorption. At a pore size less than 0.005 μm the mercury porosimetry measurements become questionable due to the high pressure required (> 60000 psi) and the uncertainty of contact angles when the diameter of the pore is equivalent to only a few atoms of mercury\textsuperscript{136}. However for this study, pore sizes below this level were regarded as unimportant.

### 3.4.2 Intrusion Measurement

There are a number of fundamental components required for mercury porosimetry measurements and these are summarised below:

(I) A penetrometer, which comprises a fixed volume compartment to contain the sample and a stem attached to the sample cell in which the mercury level varies with intrusion or extrusion

(II) Methods to evacuate the sample, to remove trapped air from the sample and to allow transfer of mercury into the sample cell.

(III) A high pressure generator, hydraulic fluid and associated apparatus to contain the penetrometer.

(IV) A probe to measure the change in mercury level with applied pressure.

Once the sample is placed in the penetrometer and mercury porosimetry apparatus the sample and penetrometer is evacuated before filling with
mercury. Once filled the pressure is gradually increased. The volume of mercury forced into the pores of a sample as a function of pressure is generally measured by the change in electrical capacitance. This is achieved by surrounding the glass penetrometer stem with a metallic shield, creating a cylindrical coaxial capacitor between the outer shield and mercury. The penetrometer is then electrically contacted to a capacitance transducer in the apparatus, Figure 25.

Figure 25: Schematic of mercury penetrometer (Micromeritics)

As the level of mercury in the penetrometer stem falls due to the sample being filled with mercury a linear decrease of electrical capacitance with increasing pore volume is observed. This electrical capacitance is converted to intrusion/extrusion volume by the simple multiplication of a manufacturer determined calibration factor. Plots of the volume of mercury intruded into the pores as a function of the pore diameter, calculated from the Laplace equation, represents the pore distribution throughout the sample. It is this information that is generally used to characterise the pore structure.
PART 2. EXPERIMENTAL
Chapter 4 CHARACTERISATION OF MARBLE SAMPLES

As established in Part 1, marble will weather under an unknown, unique set of conditions dependent on:

- **External environment, independent of the material.**
- **Characteristic properties of the material.**

It is important to have an understanding of the surface and under-lying material, since these properties will influence the development of a consolidation procedure. Since location has an important effect on the formation of patinas and alteration layers, the characterisation of actual weathered samples has been limited to those obtained from the Liverpool area and primarily the Ince Blundell collection.

**4.1.1 Materials Analysed.**

National Museums and Galleries on Merseyside (NMGM) supplied marble samples and analysis was conducted on 4 main sources within the laboratory:

1. Non-weathered Carrara Marble.

2. A leg from the sculpture of a cherub from the Ince Blundell collection originally displayed internally.

3. Marble fragments obtained from the Huskissons statue, which had been formerly located in the Liverpool City area and fragments from the Ince Blundell collection— all in varying degrees of decay.

4. A 2nd century Roman bust originally housed externally, as part of the Ince Blundell collection.
Sources 2 and 4, supplied as whole artefacts, had to be returned in good condition and hence only surface analysis techniques that require no bulk sampling could be used.

Additionally powdered Italian marble (PIM), (98% pure calcium carbonate) was used as received (English China Clays) and characterised with the above samples.

Initial work was to determine what actually required consolidation and visual examination of the above samples and sculptures still housed externally at Ince was carried out.

4.1.2 Surface Analysis of Chemical Species.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterise surface species where the surface specificity is greater for XPS compared to DRIFT spectroscopy.

4.1.2.1 DRIFT Analysis

All DRIFT spectra were recorded on a Nicolet 20 DXC spectrometer fitted with a Spectratech diffuse reflection attachment and utilising a MCT (mercury – cadmium – telluride) liquid nitrogen cooled detector. The optical bench is microprocessor controlled using Omnic version 1.2 software.

Sample preparation was dependent on the material analysed and for characterisation purposes has been performed qualitatively.

For analysis of the powdered Italian marble and extremely friable marble samples, 2.5% by weight of the sample was dispersed in ground KBr (FT-IR grade, Aldrich). The ground KBr was found to have an average particle size of 20µm. 2.5% by weight of sample was pre-determined to be the ideal sample loading for calcium carbonate, where the absorbance peak maximum was at 0.9 absorbance units. The combined sample and KBr was shaken for 5 minutes, and
lightly ground with a pestle and mortar to achieve maximum dispersion, no effect due to grinding was observed

For the weathered material and non-weathered Carrara marble where samples could not be removed and ground, the standard DRIFT technique outlined above could not be used. An abrasive method utilising a silicon carbide disc (Nicolet) was attempted. The disc was moved in circular motions over a small area four times whilst applying moderate pressure. Excess material was removed from the disc by gently tapping the disc edge on and then covered with a thin layer of ground KBr.

All samples were purged with dried air for 5min prior to recording the spectra to minimise the water vapour spectral contribution. Each sample was scanned 150 times and was automatically referenced against a pre-recorded background of KBr.

The non-weathered marble sample spectra were compared to literature results for assignment of the crystal polymorph, whilst the weathered samples were compared to experimentally measured spectra of known alteration products: calcium sulphate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Fisons), calcium sulphite hemihydrate, $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ (Synthesised in laboratory$^{137}$) and calcium oxalate (Aldrich). These standards were analysed using the standard method outlined above for powdered samples.

4.1.2.2 XPS Analysis

Spectra were recorded for the weathered Huskisson sample and for the non-weathered Carrara marble. A VG ESCALAB MK I spectrometer using Al K$\alpha$ radiation (energy = 1486.6 eV) with anode conditions of 10 kV and 20 mA under a vacuum of $10^{-7}$ torr and a take off angle of 90° was used. Analyser pass energies of 100eV and 20eV were used for the broad scan spectra and high resolution spectra respectively.

The measured binding energies are referenced to adventitious carbon (due to atmospheric contamination) at 284.6eV which allows calculation of a
correction factor compensating for the charging effect of the insulating samples. Quantification of surface species determined from the broad scan spectra was achieved by measurement of peak area after subtraction of a Shirley type background, with appropriate corrections automatically made for photoelectron cross-sections\textsuperscript{138}, attenuation length\textsuperscript{130} and angular asymmetry in photoemission\textsuperscript{139}, where appropriate.

High resolution spectra were deconvolved for the X-ray line shape, to allow for assignment of the elemental oxidation state.

4.1.3 Topographical and Bulk Physical Analysis

DRIFT and XPS analysis allowed characterisation of surface species, but also important for the development of a consolidation procedure is the physical characteristics of both the surface and bulk of the weathered samples. This was achieved by scanning electron microscopy (SEM) analysis and mercury porosimetry.

4.1.3.1 SEM Analysis

Non-weathered Carrara marble was compared to the surface of non-cleaned and laser cleaned Huskisson samples as well as upturned weathered samples to represent the highly friable areas observed on many weathered samples.

All samples were dried at 40°C and stored in a dessicator prior to analysis. Due to the insulating properties of the samples each sample was coated with a thin layer of gold before sampling, to conduct electron build up away from the surface of the material. Scanning electron microscopy and Energy dispersive analysis of X-rays (EDAX) of the weathered and non-weathered samples were run by Mr. F. Page and Mr. J. Bates in the Chemical Engineering department, Loughborough University using a Cambridge 360 SEM.

4.1.3.2 Mercury Porosimetry

Non-weathered Carrara marble and small samples weathered to varying extents from the Ince Blundell collection and the Huskisson sculpture, all non-cleaned, were analysed using a Micromeritics Poresizer 9310, software version 1 04.
Samples were dried in an oven at 40°C prior to analysis. The mass of each sample was recorded and a mercury penetrometer that was comparable to the size of sample was selected. Triply distilled mercury (Thorn) was taken to have a contact angle of 146° for calcite\textsuperscript{135}. Samples were evacuated to $5 \times 10^{-3}$ torr before filling with mercury and pore sizes between 360 – 0.005 μm were determined by automatic adjustment of pressure up to a maximum of 30,000 psi.
Chapter 5 CONSOLIDATION OF MARBLE.

5.1 Introduction

The primary aim of the research was to develop a consolidation technique that is as sympathetic to the original marble as possible. Ideally this requires the replenishment of eroded calcium carbonate to produce a less porous material, with the formation of as little by-product as possible. By-products could lead to the re-crystallisation of soluble salts, which is known to be one form of decay. Existing techniques for calcium carbonate formation as outlined in Chapter 3, have predominantly been based around the use of calcium hydroxide where the consolidatory effects remain inconclusive. This section of research has therefore been a development of this fundamental method giving consideration to the surface and physical chemistry.

An immediate problem was the lack of availability of enough samples for reproducible experimentation. Obviously it is not possible to remove large numbers of samples from one sculpture and obtaining numerous small samples from many sculptures introduces the error that no two pieces will have undergone the same set of weathering conditions. It was necessary therefore to initially try and work with model systems for the consolidation of friable areas and protection from further weathering. Proposed methods were then attempted on the small number of fragments obtained from the Ince collection and the refined method finally tested on a sculpture from the same collection.

5.2 Optimisation of Formation of Calcite From Calcium Hydroxide Solutions

The formation of crystals of calcium carbonate under an atmosphere of carbon dioxide has been studied as a function of temperature to determine crystal
polymorph and observe whether crystals are precipitated primarily in solution or at the surface / liquid interface leading to a more ordered crystal growth

**5.2.1 Materials and Experimental**

Ca(OH)$_2$ (BDH Lab Supplies) was used as received. Compressed CO$_2$(g) was obtained from BOC and regulated by a heated cylinder head. The corrected flow rate was monitored on a GPC L6X flow meter (Meterate), and the gas was heated by passing through a heat exchange coil immersed in a thermostatically controlled water bath. The gas flow was directed over the surface by the use of an inverted funnel

1ml of a saturated solution of Ca(OH)$_2$ (0.15g/100ml) in deionised water was pipetted on to the surface of a glass slide and exposed to CO$_2$ at varying temperatures and flow rates until all of the solution had evaporated. The procedure was repeated 3 times. DRIFT spectroscopy and SEM was used to determine the calcium carbonate polymorph. For analysis by DRIFT spectroscopy the precipitate was removed from the slide and analysed under the conditions set out in section 4.1.2.1., whilst for SEM analysis the samples were dried at room temperature in a dessicator.

Study of crystallisation onto a marble surface used freshly cleaved samples of Carrara marble (1cm x 1cm). The above procedure was repeated at 27°C with a CO$_2$(g) flow rate of 1 26 l min$^{-1}$. Samples were dried in a dessicator at room temperature prior to analysis by SEM

**5.3 Deposition of Calcite into Porous Media.**

A number of criteria have been considered for the application of colloidal particles to a marble surface: (1) Particle size in relation to pore size and pore distribution of extremely friable marble; (2) Stability of colloidal suspensions to the formation of aggregates and the particle / surface interactions to prevent accumulation at the outer surface; (3) Method of application to a marble surface.
5.3.1 Effect of Calcite Particle Size.

Two different sizes of calcite particles were considered in relation to the median pore diameter of weathered marble as determined by mercury porosimetry in section 4.1.3.2. Powdered Italian marble (PIM) as outlined in section 4.1.1 and precipitated calcium carbonate (PCC) (Winnofil, Zeneca) were assessed.

The surface area was pre-determined by BET nitrogen adsorption and is 4.6 m² g⁻¹ and 20 m² g⁻¹ for PIM and PCC respectively. 5% weight / volume of each type of calcite was dispersed in distilled water, and 0.2 ml of solution was pipetted onto a weathered marble surface. Where the weathered surfaces were samples from the Ince collection upturned to reveal the highly friable calcite under the surface crust. This was used to represent the base of the 2nd century Roman sculpture that required consolidation.

The samples were dried under a gas flow of dry air to aid evaporation and after 30 minutes the application was repeated. This was repeated a further two times and was followed by four applications of a clear solution of calcium hydroxide (0.2 ml) each carbonated under an atmosphere of CO₂ for 30 minutes. Samples were dried in a dessicator and analysed by SEM.

5.3.2 Particle-Particle Interaction and Particle-Pore Wall Interaction.

When applying a colloidal solution to a porous material there are many forces that determine the penetration and adherent ability of the consolidant to the bulk material. These forces include thermal motion, interparticle forces and hydrodynamic interactions. The effect of interparticle forces due to the repulsive electrostatic interaction between the decayed marble and applied colloidal solution has been studied by measuring the zeta potentials of the components and the origins of these forces are discussed thoroughly in Part 3.

5.3.2.1 Zeta Potential Measurement

Zeta potentials were determined by electrophoresis using a Malvern Zeta Master PCS. 8 mg of PCC or PIM, where the latter is taken to represent the
marble surface, were dispersed in aqueous solutions of varying alkaline pH altered by the addition of sodium hydroxide (NaOH, Aldrich). The pH was varied between 6.9 (distilled water) to 12.5. Particles were dispersed using in an ultrasonic bath prior to injection into the zeta master. An average of ten readings per sample were taken. Between each run the apparatus was cleaned with 2M HCl and distilled water to reduce cross contamination. The zeta potential was automatically calculated from the electrophoretic mobility using the Henry equation.

5.3.2.2 Colloidal stability
The stability of the colloidal dispersions at varying pH were studied as a function of dispersion method and standing time.

PCC (1.5g, Winnofil, Zeneca) was dispersed in the corresponding pH solution (30 ml) by either shaking by hand for 1 minute or dispersion in an ultrasonic bath for 15 minutes. The sedimentation volume was recorded as a function of time using a digital camera.

5.3.2.3 Application of consolidant to marble samples.
Small weathered marble fragments from the Ince Blundell collection were sprayed with varying solutions using an airbrush (Badger), and a regulated air cylinder at 5 psi (BOC):

- 5% w/v PCC dispersion at pH 10.5, 11 applications, each application dried for 20 minutes under a dry air flow.
- 0.15g l⁻¹ Ca(OH)₂ dissolved in distilled water, - 20 applications each followed with 30 minutes under an atmosphere of CO₂(g) (5 psi, 1.2 l min⁻¹ flow rate)
- 5% w/v PCC dispersion at pH 10.5, 8 applications each application dried for 20 minutes under a dry air flow, followed by 0.15g l⁻¹ Ca(OH)₂ dissolved in distilled water - 6 applications Each application followed with 30 minutes under an atmosphere of CO₂(g) (5 psi, 1.2 l min⁻¹ flow rate).
Samples were dried at room temperature in a dessicator prior to mercury porosimetry and SEM.

The surface of each sample was sprayed by passing the airbrush over the surface twice, at a distance > 5cm, this ensured that the surface did not become saturated, which would result in surface crust formation.

Application method to the 2nd century Roman bust followed the same procedures outlined above except a maximum of 6 applications per consolidant was used.
6.1 Introduction

The proposed consolidation method will not prevent further chemical weathering from acidic gases such as sulphur dioxide, since only calcium carbonate is introduced into the existing material. As such if at this stage of conservation an object was to be placed back into the environment, with a freshly cleaned surface, the rate of deterioration would continue as before and may even be accelerated. It has therefore been necessary to consider the development of a protecting layer that could be used in conjunction with the proposed consolidation method that could allow a sculpture to be placed in its original context.

The whole ethos of this research has been to be as sympathetic to the original marble as possible, such that only the necessary amount of material is applied and that this material is compatible to the original. However, a weathering protection layer means that a foreign compound has to be introduced. This section has therefore been approached with the aim to only apply a monolayer thick coating to the marble that can be applied as a single application after consolidation. This keeps the applied compound to a minimum, such that there is no pore filling and hence no effects from differences in thermal expansion, and no change in the aesthetic of the original material. Additionally the coatings tested have been derived from either naturally formed patinas or ancient treatments that were believed to hinder mechanisms of decay. Three different coatings were assessed, calcium oxalate, calcium stearate and the calcium salt of polyethylene acrylic acid.

Calcium oxalate is a naturally formed patina that is referred to as scialbatura and may take the form of wheddelite (\(\text{CaC}_2\text{O}_4\)) or whellelite (\(\text{CaC}_2\text{O}_4\ \text{H}_2\text{O}\)) and produces thick crusts from 100\(\mu\)m upwards. The conversion of the marble
and gypsum alteration layers has been studied by Mateini et al for the treatment of wall paintings and frescos by the reaction with ammonium oxalate\textsuperscript{120}. The result is the conversion of bulk material, not the formation of an additional coating, and this transformation layer has been observed to be in the order of 10\textmu m. Such a dense coating is believed to be more resistant to acid attack whilst not diminishing the wetability of the marble. These results appear promising and the application of a monolayer coating rather than the transformation of bulk material, should indicate whether the oxalate actually inhibits the mechanism of reaction or whether it is the thickness of the oxalate layer formed that slows the reaction at the oxalate/carbonate interface. The second coating, a low molecular weight polyethylene acrylic acid co-polymer is arguably the extreme of oxalic acid, where a functionalised back-bone extends further from the surface, producing a thicker coating that may inhibit the mechanisms of acid attack. Finally the third coating of calcium stearate is based on the ancient method of weathering protection where surfaces were covered with a thick layer of fat, which adsorbed into the pores of the marble and resulted in a hydrophobic surface\textsuperscript{140}. The coated samples were then tested under extreme conditions to study their effect on the weathering mechanism of ‘dry deposition’ of SO$_2$\textsubscript{g}. 

6.2 List of Materials and Chemicals

Powdered Italian marble- as described in section 4.1.1 was used as received except for grinding prior to reaction.

SO$_2$(g)- was supplied in a compressed mixture of 0.25% SO$_2$, 12%O$_2$ in N$_2$ (Air Products) and dilution of the SO$_2$ to the required concentration was achieved using compressed air (BOC)

Oxalic acid, 98% (Aldrich)

Ethylene acrylic acid copolymer 5120, (Allied Signal)

Sodium stearate (BDH purified grade)
Tetrahydrofuran THF (Fisher Chemicals)

6.3 Coating Powdered Italian Marble (PIM)

6.3.1 Experimental Procedure

1. Sodium stearate coating: PIM (10g) was coated with three differing levels of % sodium stearate by weight. These levels include 0.55% w/w, 1.1% w/w and 2.2% w/w. The PIM and sodium stearate were stirred in 250 mls of water at 80 °C for 30 minutes, samples were vacuum filtered and rinsed four times with distilled water to remove any unreacted stearate.

2. Polyethylene acrylic acid copolymer (PEAA) – PIM (10g) and 9% w/w of PEAA was stirred in THF (250ml) at 50°C for 24 hours, coated samples were vacuum filtered and rinsed four times with hot THF.

3. Oxalic acid – PIM (10g) and 0.25% w/w of oxalic acid was stirred in water (250ml) at 60°C for 24 hours

6.3.2 Analysis Procedure

DRIFT spectroscopy was carried out according to the details in section 4.1.2.1. For the 1.1% w/w coating level samples were removed every 5 minutes, dried at 40 °C and analysed by DRIFT spectroscopy. For quantitative analysis all samples were Kubelka – Munk corrected before peak integration

XPS was carried out according to the details in section 4 1.2.2. For quantitative analysis and curve fitting of the high resolution spectra all data was first deconvolved for the Al kα X-ray line shape. Spectra were peak fitted using XPS Peak Fit, Kwok version 4.1, using a Shirley type baseline.

6.4 Accelerated Weathering using SO_{2(g)}

6.4.1 Exposure Chamber Design

An experimental rig was designed that would produce a controlled humidified atmosphere at constant temperature and known concentration of SO_{2(g)} One
method of producing a known humidity is to use differing salt solutions of known vapour pressure. However, it was found that due to the rate of flow of gas over the surface a constant humidity could not be maintained. Consequently air was humidified by first saturating the gas flow, Figure 26. This was achieved by flowing the air through two dreschler bottles in series where air was introduced by using a metal frit submerged in water. This produced small bubbles that allowed quicker saturation of the air flow, after 15 minutes equilibrium 100% RH was attained.

Dry gas was then introduced via a mixing chamber to produce the required humidity such that the total flow rate of humidified air and dry air was 1 l min⁻¹ (Meterate GPE D, flow meter). The humidity was monitored throughout the experiment using a hygrometer, (Hanna Instruments, Jenson Scientific Ltd.), and was found to be stable over the 3 hour period. SO₂(g) was regulated at the cylinder by monitoring the flow rate on a flow meter (Gilmont Instruments INC.) where 175 ml min⁻¹ corresponded to 300ppm SO₂(g), once mixed with the humidified air via the second mixing chamber. Due to the corrosive nature of
the SO\textsubscript{2(g)} the humidity including the flow of SO\textsubscript{2} could not be measured. Hence after every experiment the dry air flow was increased to simulate the SO\textsubscript{2(g)} flow and the corrected relative humidity measured. All %RH values quoted are corrected values.

A back pressure release joint was placed before the flow meter thus allowing all other joints to be sealed, if any pressure built up in the system the weak joint would give and the reading on the flow meter drop.

A thermostatically equilibrated chamber was required to prevent condensation in the apparatus and all experiments were conducted at 30°C±0.5°C.

1.5 g of the non-coated or coated PIM was held in the sample chamber on a glass microfibre filter paper (Whatman)

6.4.1.1 Analysis Procedure.

Samples were taken every 30min unless otherwise stated and analysed by DRIFT spectroscopy, as outlined in section 4.1.2.1 and were Kubelka-Munk transformed before quantitative measurement. Samples were analysed no later than three days after exposure to try to minimise any changes due to air sensitivity i.e. oxidation of the sulphite to sulphate

XPS data was collected as outlined in section 4.1.2.2.
PART 3. RESULTS AND DISCUSSION
Chapter 7 CHARACTERISATION OF WEATHERED SAMPLES FROM THE INCE BLUNDELL COLLECTION

The criterion was to try and develop a consolidation technique that would be sympathetic to the original marble, by the introduction of the least amount of foreign material. This immediately precludes the organic and siloxane based polymers, which had already been classed as undesirable due to the issues of long term stability, irreversibility and laser incompatibility. In this instance an inorganic method was the only viable approach to consider. The most sympathetic would be the introduction of calcium carbonate back into the friable material where problems such as density and thermal expansion coefficient differences are avoided. In order to develop such a technique for the Ince Blundell collection, two preliminary questions were asked:

- What actually requires consolidation?
- Can a procedure be developed using a model of the weathered surface such that it reduces the risks of numerous experimental applications to actual antiquities?

Hence, before developing the calcium carbonate procedure initial consideration was given to the two questions posed above. In order to answer these questions samples from the collection were analysed by both physical and chemical techniques.

7.1 Visual Analysis of Weathering on the Ince Blundell Collection

Visual examination of various pieces from the Ince Blundell collection immediately helps to answer the first question of what requires consolidation. The effects of weathering, although resulting from a long cumulative and
complex set of parameters as discussed in Part 1, are visually apparent in a number of definable forms:

1. *Formation of a “patina”.*

2. *Formation of Black crusts.*

3. *Chemical alteration of the underlying marble resulting in cracking and lifting of surface layers.*

4. *Exposure of the friable marble to further weathering resulting in ‘sugary’ surfaces.*

The use of the term ‘patina’ tends to be applied arbitrarily to any surface that has altered from its original state, normally in terms of colour. Where, commonly, marble acquires an off white to yellow/brown coloration. Figure 27.

*Figure 27: Cherub leg showing patination on the surface.*
Examples such as Figure 27 from the Ince Blundell collection indicate that, with apparent limited weathering, the initial formation of a patina results in no perceptible loss of integrity of the marble. As a consequence no consolidation of such pieces appears to be required and only cleaning would seem necessary. The slight colour alteration observed is attributed to the soiling of the surface by atmospheric particulates, possibly with minimal chemical modification of the immediate calcite surface as discussed in section 7.2.

From visual observation of external sculpture from the Ince Blundell collection, most surfaces exhibit the typical blackened crusts that tend to accumulate on areas sheltered from the washing effect of rainfall Figure 28 and Figure 29.

![Figure 28: Mirror image carvings from the Ince Blundell Collection exhibiting varying extents of weathering](image)
The formation of black crusts and the layer immediately below have been regarded as a protective covering to the underlying marble substrate, and the question of cleaning and extent of cleaning has been debated\(^53\). Visual examination of samples from the Ince collection clearly shows weathering has not been significantly inhibited by blackened crusts. For example, Figure 28(a) and (b) are mirror image carvings located either side of the main entrance of the pantheon at Ince. (Having been exposed to the same climatic conditions they show different degrees in the extent of decay, highlighting the unique way in which every piece of marble weathers, and hence the care that must be taken when sampling and trying to make general comparisons and conclusions.) Figure 28(b) shows that the blackened layer will eventually spall away from the
material, due to the extent of weathering of the friable marble underneath this top layer, resulting in significant loss of crystal cohesion and sculptural detailing. Figure 28(a) also exhibits the normal blackened surface associated with weathering, but only initial signs of subsurface degradation are discernible in isolated areas. The thick pollutant layer may therefore reduce the rate of weathering but not totally inhibit it, and over the course of many centuries weathering must be occurring at a number of different interfaces. The general opinion is that the outer surface will continue to expand by the adsorption of pollutant particles. At the same time it is possible that the original marble surface will have undergone chemical reaction with atmospheric pollutant gases that have diffused through this top layer, or calcium ions that have leached from the bulk calcite substrate. Consequently weathering of the Ince Blundell collection has probably occurred both outwards and inwards from the original surface, effectively causing the non-weathered marble interface to retract further away from the true surface. The resulting formation of a new crystal structure, soluble salts and trapped pollutant particles, is likely to be causing increased pressure behind the black crust, which with the effects of physical weathering mechanisms, result in the lifting and loss of the surface containing the sculptural detailing. Figure 29(b), shows loss of material from under the black crust whilst Figure 29(c) shows how once this layer is removed sculptures from the Ince Blundell collection are rapidly degrading as there is almost complete loss of crystal cohesion. From these observations it is suggested that removal of the black crust is required to prevent possible increased pressure behind these layers. Consolidation is required on the highly friable areas to stabilise the remaining marble and prevent complete degradation. For sculptures such as the reliefs pictured in Figure 28, consolidation of the extremely friable areas is required before they can be removed for further cleaning and restoration.

In general the Ince Blundell sculptures exhibit zones weathered to different extents, and within one piece consolidation may be required in some areas and not others. Where only patination has occurred, and where blackened layers
have formed with no signs of lifting and cracking, consolidation is probably not required and laser cleaning need only be the form of restoration. However, where there are signs of significant alteration of the marble substrate creating what appears to be a porous interfacial layer, and where marble is exposed due to the spallation of the surface crust, some form of consolidation is required.

7.2 DRIFT Analysis of Surfaces Weathered to Varying Extents

As outlined above the loss of lustre and the formation of a new layer that is often coloured yellow is arbitrarily termed 'patina' and what actually constitutes this layer has been debated over many years\(^\text{141}\). The exact chemical composition of this surface layer will depend on the external environmental conditions that the sculpture has been exposed to and also any previous consolidation applications and artificial patination, giving to some extent a weathering history\(^\text{31,142}\). Typically the 'chemical patina' is attributed to either scialbatura, which is calcium oxalate, (either as the monohydrate whewellite, or the dihydrate wheddilite), or calcium sulphate dihydrate. It should be noted that both calcium oxalate and calcium sulphate dihydrate, when pure, are white and the yellow/brown colouring associated with the patina must arise from the inclusion of particulates during formation\(^\text{121,143,144}\).

Non-weathered Carrara marble and powdered Italian marble have been analysed by DRIFT and compared to the patina and surface of weathered samples from the Ince collection and Huskisson sculpture. Non-destructive sampling by the use of silicon carbide discs rubbed over the surface for analysis has proved a successful technique for the qualitative study of surface chemical composition and the comparison to traditional DRIFT measurement is given below.
7.2.1 Non-weathered and Powdered Marble.

DRIFT analysis of powdered Italian Marble and DRIFT (abrasive disc) analysis of the non-weathered Carrara marble, Figure 30(a) and (b) both give similar spectra. Comparison of experimental peak positions to cited literature references has allowed for complete assignment of peaks and interpretation of crystal polymorph.

Figure 30: Comparison of DRIFT sampling techniques for powdered Italian marble and quarried Carrara marble
The literature values obtained for calcite agree well with the experimental values obtained for the non-weathered marble, Figure 30. The fundamental bands at 713 cm\(^{-1}\) and 877 cm\(^{-1}\) are assigned as the degenerate bend and out-of-plane bend respectively. The large vibrational band from 1350-1650 cm\(^{-1}\) contains the fundamental degenerate stretching frequency at \(\sim 1419\) cm\(^{-1}\)\(^{149}\). Due to lowering of the crystal symmetry, a weak \(v_1\) band, assigned as the symmetrical stretching frequency, may be observed at \(\sim 1089\) cm\(^{-1}\). The additional bands are accounted for in terms of the interaction of the motion of the carbonate anion with the motion of the entire lattice of ions. In the lattice, combination of the irreducible representations of the isolated carbonate ion will be split by the anharmonic coupling of the individual fundamental vibrations. The remaining bands have therefore been assigned as follows\(^{147,148,149}\).

The maxima at 2980, 2960(sh) and 2870 cm\(^{-1}\) are the first overtone (2\(v_3\)) bands derived from the fundamental stretching (\(v_3\)) vibration of the carbonate anions in the bulk calcite structure. The bands at 2580(sh) and 2520 cm\(^{-1}\) (2513 cm\(^{-1}\) in experimental) are due to (\(v_1 + v_3\)) combination vibrations of bulk calcite. The maxima at 1790 cm\(^{-1}\) (1795 cm\(^{-1}\) in experimental) has been given a number of assignments with the most plausible being lattice vibration combination of (\(v_1 + v_2\)) in the bulk structure. Other smaller bands have also have been assigned to combination of internal lattice vibrations, although discrepancies exist with in the literature.

### 7.2.2 Weathered Marble Samples

The surface and near surface bulk chemical composition has been determined for various samples by comparison to standards typically associated with marble weathering and patina formation, Figure 31.
Figure 31: DRIFT spectra of standard alteration products associated with marble weathering.
For the cherub leg, there was found to be different coloured zones on the surface, and as a whole was non-friable so only the abrasive disc DRIFT analysis was conducted. From the DRIFT spectra in Figure 32, all the patinated areas gave similar spectra irrespective of colour. Comparison to the non-weathered Carrara marble indicates that the whole surface is still predominantly calcium carbonate in the calcite polymorph with the presence of low levels of calcium oxalate (or a highly oxidised organic species) and possibly calcium sulphate dihydrate. The colour variance must be due pollutants distributed sparsely across the surface.

![Figure 32: DRIFT analysis using abrasive disc method on varying coloured zones from cherub sculpture](image)

DRIFT analysis of the blackened patina from more severely weathered samples using both the abrasive disc technique and normal DRIFT sampling, Figure 33, shows that surface specificity is greatest using the former technique. Additionally the surface composition is no longer predominantly calcium carbonate.
Comparison to the standard spectra, has revealed the predominant component to be one compound, calcium sulphate dihydrate, (gypsum) which is in agreement with the view that marble will react to eventually form CaSO₄·2H₂O. The free sulphate ion belongs to the high symmetry point group Tₐ, in which only the triply degenerate v₃ and v₄ vibrational modes are infrared active. For monodentate co-ordination to the Ca²⁺ ion the v₁ mode becomes infrared active and the triply degenerate v₃ and v₄ modes each split into two modes. The two water molecules of crystallisation occupy different sites in gypsum resulting in three distinct stretching bands in the hydrogen bonding region and two distinct bands for the H₂O bending frequency¹⁵⁰. Table 8, summarises the peak assignment for gypsum.
### Table 8: Summary of DRIFT peak assignment for gypsum

<table>
<thead>
<tr>
<th>Frequency / cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3550</td>
<td>O-H stretch</td>
</tr>
<tr>
<td>3410</td>
<td>O-H stretch</td>
</tr>
<tr>
<td>3230</td>
<td>O-H stretch</td>
</tr>
<tr>
<td>1685</td>
<td>O-H bend</td>
</tr>
<tr>
<td>1620</td>
<td>O-H bend</td>
</tr>
<tr>
<td>1150</td>
<td>(v_3) (\text{SO}_4^{2-}) asymmetric stretch</td>
</tr>
<tr>
<td>1120</td>
<td>(v_3) (\text{SO}_4^{2-}) asymmetric stretch</td>
</tr>
<tr>
<td>1005</td>
<td>(v_1) (\text{SO}_4^{2-}) symmetric stretch</td>
</tr>
<tr>
<td>668</td>
<td>(v_4) (\text{SO}_4^{2-}) bend</td>
</tr>
<tr>
<td>602</td>
<td>(v_4) (\text{SO}_4^{2-}) bend</td>
</tr>
</tbody>
</table>

Even after laser cleaning the surface still contains a high proportion of gypsum and noticeably the chemical patina for the Ince Blundell collection and Huskisson sculpture both housed externally do not appear to contain significant levels of scialbatura as compared to the internally housed cherub sculpture.

Where no patina remains and the surface is very friable as was shown in Figure 29(c), DRIFT analysis of the crystals reveal that these areas, which require consolidation, are comprised mainly of calcite with only minimal surface alteration, Figure 34.

DRIFT analysis can therefore be used to easily distinguish between the original calcite substrate of the marble and any alteration products that exist on the surface. Additionally the use of the abrasive disc technique allows for non-destructive analysis, where this is more surface specific than actual removal of a sample followed by grinding, although the technique is difficult to reproduce quantitatively.
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Figure 34: DRIFT spectra from the 2nd Century sculpture comparing the patina to the highly friable marble on the base of the sculpture

7.2.3 XPS Analysis

XPS analysis has quantitatively identified the species present in the outermost few nanometers of the non-weathered Carrara marble and Huskisson sample, Figure 35. The results were in good agreement with the DRIFT analysis.

For the non-weathered marble, the elemental composition would be expected to be in a 1.1:3 ratio for calcium, carbon and oxygen respectively, however the elemental composition shows a higher percentage of carbon, Table 9. This is attributed to adventitious organic carbon contamination, (from the atmosphere or within the XPS instrument, such as rotary pump oil). This can be readily distinguished from carbonate carbon in the high resolution carbon 1s spectra, due to the chemical shift between organic carbon and carbon due to carbonate of ~ 4.9 eV. The tabulated core binding energy values for the Carrara marble are in good agreement to literature values obtained for precipitated calcite\textsuperscript{151,152}.

Noticeably in addition to calcium, magnesium is also present at low levels, and
is not unexpected since both elements are often found together in stone, for example dolomitic marble.

![Graph](image)

**Figure 35**: XPS broad scan spectra of Carrara non-weathered marble and weathered marble from the Huskisson statue

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron</th>
<th>B.E./eV</th>
<th>% [atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>284.6, 289.5</td>
<td>29.1</td>
</tr>
<tr>
<td>Ca</td>
<td>2p</td>
<td>347.2</td>
<td>18.5</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>531.3</td>
<td>51.8</td>
</tr>
<tr>
<td>Mg</td>
<td>Auger</td>
<td>306</td>
<td>0.6</td>
</tr>
</tbody>
</table>

**Table 9**: XPS Data for Carrara marble

The tabulated XPS data for weathered marble, Table 10, reveals the black crust to contain a high level of elemental carbon. Such a high percentage must arise due to deposition from anthropogenic sources such as fly ash and oxidised...
organic residues. The surface specificity of the XPS technique also reveals that no calcite is present in the outer few nanometers sampled, since the high resolution C 1s spectra does not have any contribution from carbonate carbon as compared to non-weathered marble, Figure 36. The measured calcium is therefore ascribed to the formation of an alteration product where the ratio of Ca to S is approximately 1:1. The measured sulphur binding energy of 169.2 eV compares reasonably well with that in the Perkin Elmer Handbook of XPS, which quotes a value of 168.8eV for sulphate binding energy. This indicates that at least the outer 2nm is predominantly gypsum with no calcium sulphite discernible. This is in good agreement to the DRIFT analysis, where the surface was found to predominantly contain calcium sulphate dihydrate.

The tabulated data for the Huskisson sample show that in addition to the presence of carbon, sulphur and oxygen, sodium chloride (NaCl) occurs with approximately 1.5% of the overall composition. This is attributed to the statue being situated in Liverpool, which has a marine environment.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron</th>
<th>B.E. / eV</th>
<th>% [atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>284.6</td>
<td>63.8</td>
</tr>
<tr>
<td>S</td>
<td>2p</td>
<td>169.2</td>
<td>3.7</td>
</tr>
<tr>
<td>Ca</td>
<td>2p</td>
<td>349.6</td>
<td>4.8</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>534.1</td>
<td>24.6</td>
</tr>
<tr>
<td>Cl</td>
<td>2p</td>
<td>198.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Na</td>
<td>Auger</td>
<td>497.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Mg</td>
<td>Auger</td>
<td>306.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 10: XPS Data for Huskisson Sample
7.2.4 Topographical and Bulk Physical Analysis

DRIFT spectroscopy and XPS has provided chemical composition data on the patinas, blackened areas and highly friable areas from the Ince Blundell collection. The physical characteristics of these areas are also important for the development of a consolidation procedure and for possible modelling of a weathered sample. Combined use of SEM and mercury porosimetry techniques of small samples give both surface topographical and bulk property information respectively, which can be used to provide data on the typical pore distribution of a whole sample.

7.2.4.1 SEM Analysis

The disaggregation on the marble surface caused by weathering is clearly evident from comparison of the surface of the Huskisson sample to that of the non-weathered Carrara marble.

Figure 36: XPS high resolution C 1s spectra of weathered marble and non-weathered marble indicating the difference in the chemical shift between organic carbon and carbonate carbon.
Non-weathered carrara marble, that has been cleaved and analysed by SEM, Figure 37, shows the sample topography to be comprised of large flat crystals of low porosity.

Figure 37: SEM image of non-weathered Carrara marble.
In comparison the SEM analysis of the blackened crust of the Huskisson sculpture shows the surface to be completely disordered and disaggregated with an obvious increase in porosity, Figure 38.

Figure 38: SEM images of polluted black crust from the Huskisson sculpture

The majority of the surface is comprised of thin crystal plates, randomly orientated producing a sponge-like porous surface. EDAX analysis, Figure 39, shows two predominant elements, sulphur and calcium and the structure has therefore be assigned to the alteration product, calcium sulphate dihydrate, which is in agreement with the DRIFT and XPS results.
Distributed intermittently across the surface are smooth spherical particles generally of two different sizes, a larger spherical particle, which is approximately 10µm in diameter, and a smaller spherical particle, which is approximately 3µm in diameter. EDAX analysis of these two different sized particles shows the predominant elemental species to be silicon and aluminium for the larger particles and iron for the smaller particles. These particles are attributed to iron oxides and aluminium/silicon oxides, which are by-products from the burning of fuels, hence the smooth spherical shape. The small amount of gold detected is due to the coating required to analyse insulating materials by SEM. Since calcium sulphate dihydrate is white, these spherical particles probably contribute to the optical darkening effect on the surface. Noticeably XPS analysis did not detect these elements and they must comprise less than 0.2% of the surface, which is generally the detection limits for the XPS technique and hence few particles are required to produce optical darkening. The SEM analysis did not reveal any bacterial or fungal colonies similar to...
those of previous studies and may therefore be assumed not to contribute greatly to the surface darkening effect.

Figure 40: EDAX analysis of spherical particles detected in the black crust on the Huskisson sculpture
When the surface has been laser cleaned fewer spherical particles are observed and the surface is less sponge-like, Figure 41. The plate-like crystals of calcium sulphate dihydrate are still present at the surface again agreeing with analysis by the abrasive disc DRIFT technique. The surface also contains small loose particles, which are most probably present due to the action of the laser cleaning process, which physically ablates the optically dark layer away from the surface. The resulting yellow coloration associated with a laser cleaned surface could possibly be due to either a small number of pollutant spherical particles remaining after laser cleaning which give the optical appearance of yellow coloration, as when a patina first forms. Or secondly due to the burning of organic pollutants present on the surface during laser cleaning.

Figure 41: SEM image of a laser-cleaned sample from the Huskisson sculpture.

The final surface of interest is the highly friable areas where no pollution crusts exist and which require consolidation for stabilisation. It was not possible to obtain a sample directly that would remain stable for analysis. Sampling was therefore conducted on upturned samples where a pollution crust existed, and
the underlying calcium carbonate, although friable, was still cohesive. SEM analyses clearly shows that the marble under the pollution crust has weathered such that individual crystals form where capillaries and channels develop around each crystal, Figure 42. For highly friable material where no sample can be taken without destroying any remaining integrity, these channels are assumed to be larger and almost completely surrounding each individual particle.

Figure 42: SEM image of weathered marble showing detached crystals.

7.2.4.2 Mercury Porosimetry

The mercury porosimetry measurements on the marble fragments, Table 11, show that as the severity of weathering increases the pore size distribution and the total porosity changes. For the non-weathered sample of Carrara marble results indicate the sample has limited porosity, calculated at only 3.3%. This is represented by a bimodal pore distribution where 59% is attributed to void spaces less than 0.1μm and can be taken to represent the natural pore spaces in
the crystal lattice structure. The larger void sizes are attributed to surface fractures that have occurred on cleaving the marble during sample preparation, additionally many carbonate rocks are regarded as naturally fractured and may contain vugs where these types of porosity are known as fracture and vugular porosity respectively\(^{153}\). Since the porosity of the non-weathered marble sample is low these natural large fracture and vugular porosity must be minimal. Notably, the mid range of pores constitutes only 8% of the total pore distribution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore distribution range</th>
<th>% of total distribution</th>
<th>% of total distribution</th>
<th>% of total distribution</th>
<th>Total %</th>
</tr>
</thead>
<tbody>
<tr>
<td>unweathered carrara</td>
<td>33%</td>
<td>8%</td>
<td>59%</td>
<td>3.30%</td>
<td></td>
</tr>
<tr>
<td>Ince collection / weathered</td>
<td>58%</td>
<td>16%</td>
<td>26%</td>
<td>29%</td>
<td></td>
</tr>
<tr>
<td>Ince collection / weathered</td>
<td>45%</td>
<td>45%</td>
<td>10%</td>
<td>5.70%</td>
<td></td>
</tr>
<tr>
<td>Ince collection / weathered</td>
<td>18%</td>
<td>56%</td>
<td>26%</td>
<td>4.50%</td>
<td></td>
</tr>
<tr>
<td>Huskisson / weathered</td>
<td>34%</td>
<td>19%</td>
<td>47%</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Huskisson weathered</td>
<td>30%</td>
<td>51%</td>
<td>19%</td>
<td>5.60%</td>
<td></td>
</tr>
</tbody>
</table>

Table 11: Pore distribution measurements for non-weathered and weathered marble samples

In comparison the most severely weathered Ince Blundell sample, has an overall porosity of 29%. Like the non-weathered sample a range of pores are present below 0.01 \(\mu\)m and are attributed to the natural inter-crystalline porosity. However, this now only contributes 26% towards the overall porosity.
of the sample compared to 59% contribution to the total porosity of the non-weathered sample. Approximately 58% of the total void volume is attributed to the largest range of pores between 100-10 μm in diameter. The remaining 16% of the total porosity is taken up by a mid-sized range of pores between the diameter of 1 - 0.1 μm. This increase in distribution towards the larger pore diameters explains the resultant decrease in cohesive strength as individual crystallites become almost completely surrounded by pore channels. It should be noted that the intrusion, extrusion data show marked hysteresis and the pore distribution will be most likely biased toward the smaller pore sizes, Figure 43. Since if larger voids or inkwell pores are only accessible from narrower entrances the pressure required to fill these pores will correspond to the pressure at the throat of the pore.

![Figure 43](image)

**Figure 43** Mercury porosimetry of severely weathered Ince Blundell sample

From Table 11, even when there has been limited weathering in terms of increase in porosity it is readily noticeable that the pore distribution changes. The original bimodal distribution of interstitial channels of the crystal lattice and surface fractures give rise to what can be assumed to be an array of
interconnecting capillaries that will increase in both numbers and depth with increased weathering.

7.2.5 Summary
Characterisation of samples has shown that the surface chemistry and physical characteristics of weathered samples are very complex. The surface patina and black crust contain high levels of calcium sulphate dihydrate in a disordered layer that incorporates pollution-derived particulates. In comparison, the friable regions where there is minimal cohesion are predominantly calcite, with large interconnecting channels forming around individual crystals. Attempts to reproduce the friable structure have not proved successful. Pressing of powdered marble gave a coherent sample but did not represent the pore structure observed on real samples. In comparison the grinding and sieving of crushed Carrara marble to give approximately the size of the individual crystals did not give a coherent structure, and their use for developing a consolidation procedure has been limited. Due to the small number of samples available a consolidation procedure was developed from theoretical principles modelled on non-weathered marble and powdered marble, to determine necessary parameters and once assessed then applied to a small number of samples.
Chapter 8 DEVELOPMENT OF A CONSOLIDATION PROCEDURE

As reported in chapter 3, many methods of consolidation exist and the most relevant procedures for the reintroduction of calcium carbonate include the use of a lime poultice based method or calcium hydroxide solution, (limewater). Considering the highly friable areas of marble from the Ince Blundell collection that require consolidation, poultice based methods would be unsuitable. Development of the traditional limewater method combined with the use of a colloidal suspension of calcium carbonate has been considered.

8.1 Calcium Hydroxide Solutions

Calcium hydroxide in solution is the ideal consolidant, as it reintroduces calcium carbonate into the bulk material with no by-products other than water

\[ \text{Ca(OH)}_2(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l) \]

However, the low solubility of Ca(OH)$_2$ (1.85 g l$^{-1}$), combined with the use of atmospheric carbon dioxide for the carbonation step has meant that it has found limited success as a consolidant$^{154}$. This can be further elaborated by simply considering the solubility of calcium hydroxide in relation to the mercury porosimetry measurements obtained from the Ince Blundell collection. Typical measurements of the more severely weathered samples from the Ince Blundell collection have given an overall porosity of approximately 30%.

From the mercury porosimetry results, the total volume of void space per gram ($V_{\text{pores}}$) is equivalent to the total intrusion volume of mercury:

\[ V_{\text{pores}} \equiv 0.112 \text{ cm}^3 \text{ g}^{-1} \]

Assuming that all the pores are equally accessible this volume will be equivalent to the maximum volume that can be occupied by the calcium hydroxide solution for any one application, such that.
\[ V_{pores} = V_{(OH)2(aq)} \]

Where, \( V_{(OH)2} \) is the maximum volume of calcium hydroxide solution. Since calcium hydroxide has a solubility of 1.85 g l\(^{-1}\) and a molar mass of 74.09 g mol\(^{-1}\) the number of moles per application can be calculated

\[
M_{(OH)2} = \frac{V_{(OH)2} S_{(OH)2}}{m_{(OH)2}}
\]

Where, \( S_{(OH)2} \) is the solubility of calcium hydroxide (g cm\(^{-3}\)), \( m_{(OH)2} \) is the molecular weight of calcium hydroxide and \( M_{(OH)2} \) is the maximum number of moles of calcium hydroxide per application that can fill the void space. If this all converts to CaCO\(_3\), the mass of carbonate formed per application can be determined and hence the volume, in cm\(^3\), occupied by the calcium carbonate:

\[
V_{CO3} = \frac{M_{(OH)2} m_{CO3}}{\rho_{CO3}}
\]

*Equation 9: Maximum volume of calcium carbonate per application*

Where, \( m_{CO3} \) is the molecular weight of calcium carbonate (100.09 g mol\(^{-1}\)), \( \rho_{CO3} \) is the density of calcium carbonate (2.71 g cm\(^{-3}\)), and \( V_{CO3} \) is the maximum volume of calcium carbonate formed per application.

For this system where the total porosity is as large as 30\%, not taking into account the geometry of the pore distribution, the total volume of pores filled by calcium carbonate per application of calcium hydroxide solution is

\[
V_{CO3} = 1.033 \times 10^{-4} \text{ cm}^3
\]

Which corresponds to an overall porosity reduction of just 0.09\%. Therefore a reduction of just 5\% in total porosity requires approximately 55 applications. This assumes that all the hydroxide applied to the weathered area enters the pore network whilst not blocking the pore throats to additional applications.
Also where atmospheric carbon dioxide is used to crystallise calcium carbonate, solid calcium hydroxide may precipitate from solution as it dries and before conversion to calcium carbonate has occurred. This would result in a slow solid state reaction, which may lead to a disordered array of crystals where carbonation is incomplete.

Taking into account the above calculation it is improbable that calcium hydroxide solution alone can be used as a consolidant, unless many applications are made. The use of limewater may allow access to and partial consolidation of some of the smallest pores, and once the colloidal suspension of calcium carbonate is applied can be used as a bridging agent to link the particles together.

The use of the calcium hydroxide solution was therefore optimised to incorporate the following objectives.

- Crystallisation as the calcite polymorph rather than the aragonite or vaterite polymorph, which are needle and disc shaped respectively. Since calcite crystals are rhombohedral precipitating the hydroxide solution in the calcite form should produce more ordered packing of the pores and channels.

- Crystallisation of calcium carbonate directly from solution, not a solid state reaction, should allow some crystals to form on surface nucleation sites. In turn this may lead to the ordered growth from the original surface.

Crystallisation, directly from solution, was carried out under a carbon dioxide environment, whilst varying the temperature and flow rate of the gas to observe the effects on the above criteria. The crystalline structure of the CaCO₃
particles formed was determined by DRIFT spectroscopy, Figure 44, and SEM, Figure 45. The results confirmed that below 40°C calcium carbonate in the calcite polymorph was the predominant species formed under static conditions, rather than aragonite or vaterite. Additionally the lack of any calcium hydroxide in the DRIFT spectra indicates that calcite was formed directly from solution before evaporation of water. At a temperature above 40°C, the product is still predominantly calcite although there appears to be some needle like crystals that are attributed to aragonite formation, Figure 46. Crystallisation onto the glass slide indicates that the formation of the crystals occurs around small nuclei rather than spontaneous deposition of many small individual particulates due to the high CO$_2$(g) concentration.

![Figure 44: DRIFT spectra of starting material and crystallised product after reaction with CO$_2$(g)](image-url)
Figure 45: SEM images of calcite formed at (a) 27 °C and (b) 40 °C.

Figure 46: SEM image of calcite and possibly aragonite formed at 60 °C.

The growth of calcium carbonate crystals onto cleaved non-weathered marble also indicates that calcite is the predominant crystal form produced. The optimum flow rate of gas was observed to be between 1.26 l min\(^{-1}\) and 2.2 l min\(^{-1}\) of CO\(_2\) at room temperature. After the first application of the calcium
hydroxide solution, some areas appear to show ordered growth from the surface, indicating that crystallisation occurs at the marble surface and grows outwards. If precipitation occurred in the solution layer the calcite would be expected to deposit randomly on the surface after evaporation of water.

Figure 47: Growth of calcite crystals on the surface of non-weathered marble.

Once surface growth has initiated it appears that continued crystallisation tends to occur on these sites leading to columns of new growth that bridge across to other columns giving a less ordered structure. Calcite nucleation studies have
reported that crystals do tend to form agglomerates in stirred solutions, where the crystals bond and grow into one another\textsuperscript{155}. Additionally directionally orientated growth of calcium carbonate has been observed at charged organic monolayers\textsuperscript{156,157} For crystallisation to occur the dissolved ions have to accumulate and then arrange themselves in a crystalline pattern to form a nucleus, and nucleation can be promoted by a structured surface, which offers a template and may influence the lattice structure\textsuperscript{158,159}. For the present system, the calcite surface will become charged in the presence of an aqueous solution and will lead to a high concentration of ions near to the surface and hence preferential surface nucleation is feasible Charged interfaces are discussed fully in the following section.

It is acknowledged that using an atmosphere of CO\textsubscript{2}(g) could lead to dissolution of surface calcium carbonate, however a number of factors should be considered. Table 12, gives the amount of CO\textsubscript{2}(g) dissolved in water (g l\textsuperscript{-1}), as a function of CO\textsubscript{2}(g) partial pressure and in theory how much calcium carbonate could dissolve.

<table>
<thead>
<tr>
<th>CO\textsubscript{2} content of atmosphere (% vol)</th>
<th>CO\textsubscript{2} dissolved (g l\textsuperscript{-1})</th>
<th>CaCO\textsubscript{3} dissolved (g l\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 Normal air</td>
<td>0.00054</td>
<td>0.014</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0054</td>
<td>0.14</td>
</tr>
<tr>
<td>1</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>10</td>
<td>0.18</td>
<td>0.47</td>
</tr>
<tr>
<td>100 CO\textsubscript{2} at atm. Pressure</td>
<td>1.8</td>
<td>1.06</td>
</tr>
</tbody>
</table>

\textit{Table 12: Solubility of carbon dioxide and calcium carbonate at various partial pressures of CO\textsubscript{2}}

At 100\% CO\textsubscript{2}(g) the amount of dissolved carbon dioxide is 0.03 M assuming all the gas penetrates into the pores, which will not be the case. The applied solution contains 0.025 M calcium hydroxide and the initial stages will result
predominantly in the crystallisation of calcite rather than dissolution. The crystallisation steps are shown in Figure 48, where calcite dissolution is also considered. It should be noted that the reaction between \( \text{CO}_2(\text{g}) \) and dissolved \( \text{Ca(OH)_2} \) involves numerous steps including the gas-liquid mass transfer of \( \text{CO}_2(\text{g}) \) and its hydration, chemical reaction between bicarbonate and hydroxyl ions as well as nucleation and growth of calcium carbonate crystals\(^{160}\). The action of \( \text{CO}_2(\text{g}) \) blown over the surface also aids evaporation of the liquid phase and re-crystallisation of calcite must occur with no net loss of material maybe just redistribution. The study at lower partial pressures of \( \text{CO}_2(\text{g}) \) would be interesting although the main aim is to grow the calcite directly from solution.

\[
\begin{align*}
\text{CO}_2(\text{g}) + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 + \text{Ca(OH)_2} & \leftrightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \\
\text{H}_2\text{CO}_3 + \text{CaCO}_3 & \leftrightarrow \text{Ca(HCO}_3)_2 \\
\text{Ca(HCO}_3)_2 + \text{Ca(OH)_2} & \leftrightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}
\end{align*}
\]

Figure 48: Crystallisation reaction of calcium hydroxide with carbon dioxide\(^{78}\).

8.1.1 Summary on Calcium Hydroxide Solutions
Crystallisation has been shown not to result in a random array of precipitated calcium carbonate but form well defined crystals. Typically, at the observed optimum flow rate of \(~1.3\ \text{l min}^{-1}\), crystals can be grown onto the surface where the typical size is between \(0.5 - 1\ \mu\text{m}\). In terms of application to a weathered surface, the solution should be applied sparingly such that the bulk material does not become saturated and hence prevent pore blocking. Carbon
dioxide can then be applied after allowing the solution to be absorbed into the porous material due to capillary action.

Even allowing for optimisation of the carbonation step in carbon dioxide rich environments and crystallisation onto the marble surface, the number of applications required to bring about a known porosity reduction (i.e. 0.09%), can not be less than that predicted by Equation 9. To reiterate, such a large number of applications make the use of hydroxide solutions as the sole method of consolidation impractical. Another method or complementary method of introducing calcium carbonate into the bulk material is required. Obvious solutions may have been to use a different calcium ion source, of higher solubility, and perform an ion exchange reaction as outlined in part 1. The immediate drawback to this is the introduction of an additional reaction product such as sodium chloride or an ammonium salt, foreign to the original material. These soluble salts are prone to migration to the surface where the action of salt efflorescence may predominate. An ideal situation would therefore be to directly introduce calcium carbonate, as calcite, into the friable material. Since calcium carbonate has a low solubility it would have to be applied in the particulate form. Consideration therefore has to be given to the areas of particle size in relation to pore sizes, how to get the particles to penetrate the surface layers and the method of particle application. Such considerations are of paramount importance, to avoid a paste type application where a surface crust is formed.

The overall aim is to use calcite particles to partially fill the larger pores and void spaces, whilst calcite grown in situ from $\text{Ca(OH)}_2(\text{aq})$ and $\text{CO}_2(\text{g})$ can be used to reach the smaller deeper pores and act as a bridging agent across the applied particles to the original material. A combination of both approaches should reduce the overall application number compared to using calcium hydroxide solutions alone.
8.2 Deposition of Calcite into Porous Media

To prevent the applied CaCO$_3$ becoming little more than a paste or poultice that results in the blocking of surface pores and the formation of thick unsightly overlayers, careful consideration and control of a number of factors are required:

1. **Particle size of the applied CaCO$_3$ in relation to pore sizes and pore distribution of the marble surface.** If the diameter of the applied CaCO$_3$ particles is of the order of the surface pore diameter, accumulation at the surface will occur.

2. **Particle–particle interaction in the dispersion medium and particle–pore wall interaction during application.** The dispersion must remain sufficiently stable to allow application of the CaCO$_3$ before sedimentation or aggregation of the particles occurs. Additionally they must be easily re-dispersed for later applications. Secondly the particle–surface interaction must be such that the particle does not preferentially accumulate on the surface due to point of first contact.

3 **Application method of suspension.** Since the cohesion of the existing fabric is low, application of the dispersion to the surface should not cause loss of further material.

8.2.1 Particle Size of the Applied CaCO$_3$ in Relation to Pore Size at the Marble Surface and Near Surface.

From the characterisation of the marble samples, the areas typical of the base of the 2nd century Roman bust are the most friable requiring stabilisation. The
porosity of this region has most likely arisen due to a combination of physical weathering, such as thermal cycles, and dissolution and movement of ions from the crystal lattice due to water ingress into the bulk material. The resultant effect will probably be a variety of randomly distributed pores and channels of various sizes. Some of which inter-connect to form a continuous phase and some of which are non-interconnected to form dead-end or blind pores, but all that narrow with depth until the bulk of the non-weathered marble is reached. The relationship of the applied calcium carbonate to this pore size distribution is fundamental to the proposed method of consolidation. It is important to select a calcium carbonate particle that is small enough to penetrate the surface and desposit deep into the pore distribution.

The mercury porosimetry results for the weathered samples given in section 7.2.4.2, indicated that the mid-range of pores are evident only in the weathered samples and are therefore attributed the formation of the interconnecting channels and pores. In terms of the consolidation procedure the important result from the pore distribution of the analysed samples is the mean pore size for each distribution range as given in Table 13. These mean values can be used to determine the ideal size for applied particles.

From the pore distribution results it was observed that the weathering process resulted in an increase in the largest pore size distribution range and additionally an increase in pore size making up the 10 – 0.1 μm range. This latter range of pores gave a mean pore diameter between 4.2 μm to 2.6 μm dependent on the sample. Hence the applied particle size should be such that it is small enough to penetrate this range of pores where the pores can be considered as constituent to both the surface and subsurface capillary network.
Table 13: Mean pore diameter of weathered marble samples as determined by mercury porosimetry for the three main distribution ranges.

Calcium carbonate particles, as the calcite polymorph, can be obtained two ways, firstly natural calcite, such as marble, that has been powdered and sieved to a known particle size range or secondly, synthetically precipitated calcium carbonate. Powdered Italian marble from English China Clays has been measured by BET nitrogen adsorption and has a mean surface area of 4.3 m² g⁻¹ with no porosity, this corresponds to an individual particle diameter of ~ 0.51 μm as estimated from Equation 10

\[
SA = \frac{3}{ap}
\]

Equation 10: Surface area
Where SA is the surface area ($m^2 \text{ kg}^{-1}$), $a$, is the particle radius (m) and $\rho$ is the density ($kg \text{ m}^{-3}$).

BET nitrogen adsorption of the precipitated calcium carbonate (PCC) provided by Zeneca gave an average particle surface area of $20 \text{ m}^2 \text{ g}^{-1}$ which corresponds to a particle diameter of $0.11 \mu m$. It should be noted that both particle diameters are indicative of the individual particle size and the particles most likely exist as agglomerates.

PCC is approximately 4.6 times smaller than the natural calcite, with both sizes smaller than the median pore diameter of the range of pores attributed to weathered marble. It would suggest therefore that either PIM or PCC could be used in the consolidation procedure. However, Barkman and Davidson\textsuperscript{161} have studied the impairment of water flow through porous media due to action of suspended solids and calculated the effect of particle diameter in relation to the pore size distribution. In general three mechanisms occurred as outlined below and in Figure 49.

1. Particles larger than one-third of the pore diameter, bridge the pore entrance at the surface leading to the formation of an external filter cake.

2. Particles smaller than one-third of the pore diameter, but larger than one-seventh penetrate the surface and are trapped internally forming an internal filter cake.

3. Particles smaller than one-seventh of the pore diameter cause no impairment of water flow since they are carried through the pore network, although gradual blocking can occur.
Both particle sizes are less than one-third of the smallest median pore diameter (2.6 μm), which suggest that surface caking would not occur. However, for the PIM if only two particles are aggregated the combined diameter exceeds one-third of the pore size and pore blocking leading to surface crust formation may occur. For the PCC an aggregate of 8 particles would be required to exceed this value.

SEM analysis of a weathered sample from the Ince Blundell collection, where the particles have started to lose cohesion, show that the gaps forming around the individual crystallites have a diameter of ~6μm, Figure 50. 5% solutions of the two different sized particles in distilled water were applied to the surface by a pipette, followed by the addition of calcium hydroxide solutions. Figure 51 and Figure 52, show the effect of particle size on the accumulation and development of surface crusts for PIM and PCC respectively.
Figure 50: SEM images of weathered Ince marble (a) low magnification (b) High magnification
Figure 51: SEM images of weathered Ince marble treated with marble powder followed by Ca(OH)$_2$ solution (a) low magnification (b) high magnification.
Figure 52: SEM images of weathered Ince marble treated with PCC followed by Ca(OH)$_2$ (a) low magnification (b) high magnification
The SEM images show that the powdered marble blocks the pores. The application of the calcium hydroxide solution followed by carbonation has led to the formation of a dense crust due to lack of penetration, which appears to have cracked on drying and is assumed to be hard and brittle. In comparison, the smaller particle size appears to have coated the surface more evenly and it is assumed has penetrated into the subsurface, to some extent. Application of the calcium hydroxide solution has not formed a brittle crust presumably because the applied PCC has not formed a dense array of packed particles, but an open network, which allows penetration of the calcium hydroxide solution.

The measured median pore diameters for weathered marble combined with the initial application of the two particle sizes to a weathered surface, show the necessity for careful selection of materials. Although both particle sizes were smaller than the median pore diameter issues such as particle tendency to form agglomerates in solution and how these interact with the marble surface are raised. The PCC due to its smaller particle size was selected as the material to be used for further study as a consolidant, and issues such as colloid stability, particle/surface interaction and application method were considered.

8.2.2 Particle–Particle Interaction in the Dispersion Medium and Particle–Pore Wall Interaction During Application

Application of calcium carbonate, (PCC), to weathered marble requires dispersion in some medium so as to allow for the flow of particles through the pore network. To keep the number of applications as low as possible, with each application sufficient to cause a significant decrease in porosity, a specific percent weight of PCC to volume of dispersing medium (%W/V) needs to be specified. This should be such that the overall viscosity of the dispersing medium remains constant with the individual particle motion during transport being governed by thermal and hydrodynamic forces. Hence assuming that the particles remain equally dispersed a 5% W/V dispersion should cause a 5% reduction in void space of the friable material per application, if all of the pore
distribution is accessible to the size of the particles. This is 55 times greater than the reduction in void space per application of a calcium hydroxide solution. There are a number of phenomena that predominantly influence both the size of the particles in the dispersion medium and the interaction of particles with the marble substrate. Without knowledge and control of these interactions a reduction in the overall effectiveness of the dispersion method may occur.

8.2.2.1 Theoretical Consideration

For a 5% W/V dispersion of PCC in water, where the particles are regarded as moving freely due to Brownian motion only, the number of collisions between particles and the time between these collisions can be easily estimated\(^1\)\(^6\)\(^3\).

\[ t_c = \frac{D}{v} \]

Where \(t_c\) is the time between collisions in seconds, \(D\) is the mean separation distance in metres and \(v\) is the Brownian velocity of a particle in \(\text{m s}^{-1}\). Taking the radius of particles to be 55 nm and the energy for Brownian motion to be equivalent to the translational kinetic energy, which is approximately \(3/2kT\), the velocity of particles is equal to:

\[ v = \sqrt{\frac{3kT}{m}} \]

Equation 11: Brownian velocity

\[ = 0.08 \text{ m s}^{-1} \]

Where \(m\) is the mass of one particle of calcium carbonate (1.9 x 10\(^{-18}\) kg) estimated from the volume of one particle and the density of calcium carbonate (\(\rho = 2710 \text{ kg m}^{-3}\)). The number of particles per unit volume is therefore equal to the total mass of particles divided by the mass of one particle. Hence the
mean surface to surface separation distance can be obtained from the volume of water surrounding one particle (which is the corrected unit volume of solvent divided by the number of particles per unit volume), taking into account the finite size of the particle:

\[ D = 2 \left( \frac{\sqrt[3]{V_s + V_p} - 2a}{2} \right) \]

Equation 12: Theoretical separation distance between particles

\[ D = 2.3 \times 10^{-7} \text{ m} \]

\[ D/v = 2.88 \times 10^{-6} \text{ s} \]

Where \( D \) is the mean distance between particles, \( V_s \) is the volume of solution around one particle, \( V_p \) is the volume of one particle and \( a \) is the radius of a particle. Thus the time between collisions, \( (D/v) \), at room temperature is approximately 2.88 x 10^{-6} s equating to 7 x 10^6 particles colliding every second. Thus, random Brownian motion results in numerous encounters between particulates, and the stability of the PCC dispersion and deposition of PCC onto the marble surface is dependent on how the particles interact when these encounters occur.

8.2.2.2 DLVO Theoretical Effect on Particle and Marble Interactions

When the distance between particles and between particle and pore wall are less than the particle radius, fundamental forces take over from Brownian motion, combining to determine interfacial interactions. These forces of interaction primarily include the London-van der Waals dispersion forces, which are attractive and exist between all bodies and the electrostatic repulsive forces resulting from the formation of an electrical double layer. The resulting interaction potential has been formulated into the well-known DLVO theory. Named after Deraguin and Landau and Verwey and Overbeek who
independently quantified the description of colloidal stability, both forces are assumed to be additive and combine to give the total energy of interaction as a function of interparticle distance.

\[ V_{tot} = V_A + V_R \]

Equation 13: Total energy of interaction

Where \( V_A \) is the potential energy of attraction, \( V_R \) is the potential energy of repulsion and \( V_{tot} \) is the total potential energy of interaction. The result is an energy versus separation profile that predicts how two specific bodies will interact as transport mechanisms bring them within the range where interaction occurs, Figure 53.

![Figure 53: Schematic diagrams of repulsive and attractive free energy which when summed result in a total energy of interaction profile vs separation distance where plots (a), (b) and (c) represent possible interactions](image)

In terms of the application of PCC to a weathered marble surface a number of possibilities may arise as outlined below, with the potential effect on the overall consolidation procedure discussed.
Where the attractive potential energy predominates (Figure 53(a)), the free energy of interaction is negative over a “long range” causing a net attraction between particles. This results in most collisions causing particles to enter a deep primary minimum. This is manifested by the rapid aggregation of particles, which move more slowly encountering other particles and hence effectively increasing in mass until they rapidly sediment out due to gravity or adhere to the pore wall. (It should be noted that aggregation is the loss of a species kinetic independence rather than individual properties of the particle, such that a cluster of particles moves as one unit but with little change in total surface area.) This rapid aggregation of particles into a deep primary minimum is known as coagulation, and is characterised by a compact sedimentation volume that tends to be difficult to re-disperse Figure 54(a).

Rapid coagulation would be undesirable for the use of PCC as a consolidant, since the aggregates formed rapidly are held in a deep primary minimum where a large amount of energy is required to re-disperse them into individual particulates small enough to flow into the pore network. Application of such a system would most likely lead to the formation of surface layers since the effective particle size is increased to such an extent that the particle cannot penetrate the surface.

From Figure 53(b), \( V_R \) can be greater than \( V_A \) at a moderate separation distance producing a positive potential energy barrier to coagulation, hence the particles repel one another resulting in a kinetically stable state. The kinetic stability of the dispersion will depend on the height of the energy barrier in relation to thermal energy \((kT)\). Where the energy barrier is greater than \( kT \) only a fraction of the collisions result in aggregation and the colloidal system is classed as stable. Such a system would be ideal for consolidation since the PCC will remain as individual particulates for longer and if the same profile exists between PCC and marble the interfacial energy is minimal during transport. Hence if \( V_R \) is not too great the PCC would be repelled from the
marble surface and be forced through the pore network reducing the tendency of surface layer formation.

A third possible interaction profile arises from the difference in distant dependency of the van der Waals and electrical double layer forces. They vary according to the power law and exponential law respectively. This results in the attractive potential tending to be greater at large separations, which in turn can lead to the formation of a secondary minimum (Figure 53(c)). Where this is of the order of $kT$ the formation of weak voluminous aggregates that are readily reversible occur. This state is known as the flocculated state (Figure 54(b)). The effective increase in mass as particles aggregate, will enhance the sedimentation rate. Although not as ideal as a stable colloidal dispersion, the particles are only held in a secondary minimum by a weak attraction and so long as the aggregates are dispersed by some means during application flow into the pore network should still occur.

![Figure 54: Sedimentated particles; (a) in a primary minimum - coagulation (b) in a secondary minimum - flocculation](image)
Generally, it should be noted that other non-DLVO forces could arise, which at short separation distances, less than a few nanometers, accounts for the deviation of the DLVO prediction from experimental observations. These short range forces include hydration forces and Born repulsion and are intrinsic to the solvent and particle surface. Secondly longer ranged repulsion forces can arise from a steric force due to the presence of an adsorbed macromolecule or surfactant at the interface, leading to a stable colloidal dispersion due to entropic effects of mixing. This external control forms a large body of research in colloidal stability. For the development of the consolidation procedure the use of surfactants and polymeric stabilisation introduces an additional compound to the sculpture and secondly increases the particle radius, which may act to block the surface pores of the friable material. Hence the study of the colloidal interaction and particle-pore wall interaction has been limited to minimal external manipulation.

8.2.2.3 Experimental Determination of Interaction energy

The electrostatic forces and to some extent the dispersion forces are dependent on the particle surface and solution chemistry. Hence the control of physiochemical parameters such as particle size, surface charge, solution pH and electrolyte concentration all govern the magnitude and type of interaction profile. An understanding of each of these parameter's influence and possible manipulation is therefore important for the use of solid particulates as part of the consolidation procedure. Hence, before arbitrarily applying a PCC dispersion to the weathered marble surface a predictive model is required for the quantitative description of the fundamental forces for particle-particle and particle-pore wall interaction. The most promising set of conditions resulting from the predictive model have then be applied in reality to the friable area on the 2nd Century Roman sculpture from the Ince collection.
The electrostatic interactions ($V_R$) are discussed first followed by the dispersion forces ($V_A$). Finally the total energy of interaction is calculated and compared to qualitative experimental observations for the particle-particle interaction. The descriptive model is assumed for the PCC-pore wall interaction and compared to the results obtained from the consolidation of the Roman sculpture.

The following sections cover the background to the origin of many colloidal principles and although this is well reviewed in the areas of colloidal and polymer science the application to conservation has not been fully investigated. Hence fundamental principles are outlined within the results and discussion to set the foundation for the development of the new method for consolidation.

### 8.2.2.3.1 Electrostatic Force Contribution to $V_{total}$

Electrostatic forces originate from the tendency of inorganic materials to acquire a surface charge in a polar medium. Three parameters are required for determination of $V_R$:

1. **The particle radius**, already pre-determined.
2. **Surface potential** ($\psi_0$) estimated from electrokinetic methods.
3. **The diffuse layer thickness** ($1/\kappa$), dependent on ions in solution.

The latter two parameters are defined by the electrical double layer (EDL) and as the terminology suggests is comprised essentially of two regions.

1. **The charged surface.**
2. A neutralising excess of counter-ions over co-ions, spatially distributed according to the opposing influences of: (a) electrostatic attraction of counter-ions to the surface and (b) random distribution due to thermal energy. Hence the term diffuse layer.
Unequivocal determination of these two regions is not possible and many assumptions are made. The potential throughout the diffuse double layer can be estimated and the general equations most commonly encountered for the description of the potential in these layers are given below. For simplicity the pore wall is taken to be a flat surface since the pore diameter is large compared to the particle size. Hence the potential at any point \( x \) in the diffuse layer is defined by the Poisson-Boltzmann equation developed by Guoy and Chapman, Equation 14. A complete description is given in appendix 2:

\[
\psi = \frac{2kT}{ze} \ln \left( \frac{1 + \gamma \exp[-\kappa \psi]}{1 - \gamma \exp[-\kappa \psi]} \right)
\]

**Equation 14: Poisson-Boltzmann equation**

Where

\[
\gamma = \frac{\exp[ze \psi_0 / 2kT] - 1}{\exp[ze \psi_0 / 2kT] + 1}
\]

Where \( z \) is the charge number on the ion, \( e \) is the electron charge, \( k \) is the Boltzmann constant and \( T \) is the temperature and \( \kappa \) is the Debye-Hückel parameter.

For low potentials the Poisson-Boltzmann distribution is often approximated using the Debye-Hückel linear approximation, Equation 15.

\[
\psi = \psi_0 \exp[-\kappa \psi]
\]

**Equation 15: Debye-Hückel approximation for flat surfaces**

For a spherical particle the potential at any point \( r \), radially from the surface in the diffuse double layer cannot be analytically solved and the linear approximation for low surface potential is given by Equation 16.
If \( I_{-} = I_{+} = 0 \) \( \sim \exp[-K(r-a)] \)

Equation 16: Debye-Huckel approximation for spherical interfaces

Where \( a \) is the particle radius. Generally the potential in a diffuse layer is found to fall approximately exponentially from the surface.

It is the overlap of two diffuse layers that causes repulsion when two bodies of like charge interact, conversely when two dissimilar bodies interact attraction can occur leading to mutual coagulation. Hence electrostatic interaction can be either attractive or repulsive.

8.2.2.3.2 Determination of Calcite Surface Potential.

Considering first the surface charge, it is important to impart a charge that results in both the surface of the marble and the PCC having the same charge sign, such that electrostatic repulsion rather than electrostatic attraction occurs both between particles and between the particle and pore wall. For calcite this has been achieved by altering its solution chemistry.

The charged surface is characterised by two fundamental electrical properties, the surface potential \( \psi_0 \) (V), and the surface charge density \( \sigma_0 \) (C m\(^{-2}\)). The approximate relationship at low potential is given in Equation 17, for flat surfaces and Equation 18, for spherical surfaces.

\[
\sigma_0 = \varepsilon_0 \varepsilon \kappa \psi_0
\]

Equation 17: Surface charge density on a flat surface

\[
\sigma_0 = \frac{\varepsilon_0 \varepsilon \psi_0}{a} (1 + \kappa a)
\]

Equation 18: Surface charge density on spherical surface

Where \( \varepsilon_0 \) is the permittivity of free space and \( \varepsilon \) is the dielectric constant of the medium.
From the above equations the surface potential depends on both the surface charge density and through $\kappa$ the ionic composition of the solution, (as discussed in the next section).

The surface potential for calcite was determined by measurement of the zeta potential, ($\zeta$ mV) as a function of pH, altered by the addition of sodium hydroxide. The zeta potential again only gives an estimate of the surface potential due to the ambiguity in the actual surface location. Counter ions can only approach a surface to within their hydrated radius and this limit of approach is known as the Stern plane (or outer Helmholtz plane). If an ion can become dehydrated at least in the direction of the surface, ions can reside in the Stern layer and are effectively adsorbed. The boundary limit of closest approach (ionic radii) is known as the inner Helmholtz plane$^{164}$. The Stern plane is termed $\psi_d$, where ions beyond this boundary form the diffuse layer. $\psi_d$ generally replaces $\psi_0$ in the previous equations and the zeta potential, $\zeta$, which is the potential at the surface of shear between the charged surface and electrolyte solution is taken to be approximately equivalent to $\psi_d$. It should be noted that the zeta potential is likely to be slightly smaller than $\psi_d$ since the plane of shear lies just outside of the Stern plane due to water of hydration on bound ions.

Normally when studying colloidal dispersions the ionic strength of the solution is kept constant by an indifferent electrolyte, such as chlorides and nitrates. However, the main principle here is to minimise the amount of foreign material applied to a sculpture and the use of sodium hydroxide was deemed the maximum external influence permissible.

Figure 55 and Figure 56, for PCC and PIM respectively give the measured zeta potential as a function of pH. PIM was used to represent the marble surface, since calcite was the main species determined by DRIFT on the highly friable regions of the 2nd century Roman bust from the Ince Blundell collection. To ensure that the model samples were representative of actual sculptural marble...
two samples were taken from the Ince Blundell collection. The first sample was ground marble from a highly friable surface, that PIM is used to represent. The second sample was ground from a black crust fragment. A zeta potential in distilled water of 1 mV and -18.7 mV respectively was observed. The tendency for low to negative surface potentials correlates well to the results on the model systems.

Figure 55: Zeta potential measurements for PCC as a function of pH where the solution was equilibrated for 7 days
A number of points can be raised from these results:

1. The addition of both PIM and PCC to the solutions caused an alteration in the overall pH. At an initial pH below 8.5 addition of calcite resulted in an increase in pH, where for distilled water the pH was observed to increase from 6.9 to 8.06 for PCC and from 6.9 to 8.7 for PIM. An equilibrium pH of
approximately 8.3-8.4 has been reported for water in equilibrium with calcite and air and compares reasonably well to these results\textsuperscript{168}. At a pH above 8.5 addition of calcite was observed to result in a reduction in overall pH of the solution. These results compare to the findings of Somasudaran and Agar\textsuperscript{165} where the pH changes are dependent on the dissolution of calcium carbonate and the corresponding concentration of species in bulk solution and the formation of surface complexes. Since calcium carbonate is sparingly soluble, its addition to water results in the dissociation of Ca\textsuperscript{2+} and CO\textsubscript{3}\textsuperscript{2-} ions producing a more alkaline solution. At higher initial pH the dissolution of calcite results in the formation of complex solution species with reduction in free hydroxyl ion concentration and hence a decrease in pH.

2. The slight differences in zeta potential between the two samples can be explained by differences in equilibration time. PCC was equilibrated for a minimum of 7 days whilst PIM measurements were made with minimal standing time. In order to try and replicate conditions for an actual consolidation procedure consideration was given to contact times of the CaCO\textsubscript{3} with the aqueous phase. The applied PCC dispersion can be prepared in advance of application allowing equilibration of the solution species whereas the marble surface will only contact with the solution on application of the consolidant. (It should be noted that the marble surface would probably already have a localised surface charge due to inherent water condensed in the pores and capillaries.). Somasundaran and Agar\textsuperscript{165} and Siffert and Fimbel\textsuperscript{168}, observed a long equilibration time for calcite, which in turn resulted in slight shifts in the observed zeta potential.

3. The general trend for both species is that the zeta potential decreases with increasing alkalinity of the solution giving a positively charged surface in water and a negatively charged surface in the presence of NaOH. The surface electrical properties of calcium carbonate, as calcite, have been extensively studied under varying conditions giving rise to many inconsistent and apparently contradictory results\textsuperscript{166,167}. This tends to arise due to calcite strongly
influencing the surface charge and hence electrokinetic potential and small differences in experimental conditions can give significant differences in results\(^{168}\). Calcite has limited solubility in water (0.014g dm\(^{-3}\)) and there are a large number of reaction possibilities that describe dissolution and interaction of the chemical species produced when calcium carbonate is dissolved in water\(^{165,169}\), Figure 57.

\[
\begin{align*}
\text{H}_2\text{CO}_3, \text{HCO}_3^{-}, \text{CO}_3^{2-}, \text{Ca}^{2+}, \text{CaHCO}_3^{+}, \text{CaOH}^{+}, \text{Ca(OH)}_2(\text{aq}), \text{CaCO}_3(\text{aq}).
\end{align*}
\]

\[
\begin{align*}
\text{CaCO}_3 & \leftrightarrow \text{CaCO}_3(\text{aq}) \\
\text{CaCO}_3(\text{aq}) & \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \\
\text{CO}_3^{2-} + \text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^{-} + \text{OH}^{-} \\
\text{HCO}_3^{-} + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 + \text{OH}^{-} \\
\text{H}_2\text{CO}_3 & \leftrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O} \\
\text{Ca}^{2+} + \text{HCO}_3^{-} & \leftrightarrow \text{CaHCO}_3^{+} \\
\text{CaHCO}_3^{+} & \leftrightarrow \text{H}^{+} + \text{CaCO}_3(\text{aq}) \\
\text{Ca}^{2+} + \text{OH}^{-} & \leftrightarrow \text{CaOH}^{+} \\
\text{CaOH}^{+} + \text{OH}^{-} & \leftrightarrow \text{Ca(OH)}_2(\text{aq}) \\
\text{Ca(OH)}_2(\text{aq}) & \leftrightarrow \text{Ca(OH)}_2(\text{s})
\end{align*}
\]

Figure 57: Calcium carbonate species formed when dissolved in water open to the atmosphere\(^{165}\).

Although such a complex dissolution mechanism exists for calcite, the hydrated Ca\(^{2+}\), CO\(_3^{2-}\) and HCO\(_3^{-}\) ions are generally considered to be the major potential determining ions (PDI) and OH\(^{-}\) and H\(^{+}\) are regarded as secondary PDI. Potential determining ions give rise to the electrical charge and charge sign of the mineral surface due to back adsorption. The electrokinetic potential is therefore governed by the concentration of these free ions in solution, which in turn is related to the pH of the solution. Thompson \textit{et al} amongst others\(^{165,170}\) have compiled from equilibrium constants, the influence of pH on the concentrations of ionic species in saturated aqueous solutions of calcite open to atmospheric carbon dioxide (pCO\(_2\) = 3.3 x 10\(^{-4}\) atm), Figure 58.
From Figure 58, and the experimental data it is possible to postulate the mechanism of charge generation for the calcite surface. For most inorganic species in water the charge on the surface is negative, because the cations tend to hydrate more than the corresponding anions and hence reside in the bulk solution. The less hydrated anion can back adsorb onto the surface giving a negative charge. However for calcite the surface charge is positive in water and can be attributed to presence of an excess of divalent Ca$^{2+}$ ions over free CO$_3^{2-}$ ions. In the presence of divalent cations the surface concentration is much higher than would be for monovalent cations. Therefore divalent ion binding occurs which leads to charge reversal.

In the presence of sodium hydroxide the zeta potential becomes negative increasing with pH and from Figure 58, the concentration of both free CO$_3^{2-}$,
HCO$_3^-$ and OH$^-$ at equilibrium increase with pH as the concentration of free Ca$^{2+}$ ions decrease. Hence back adsorption of the carbonate ion results in a negatively charged surface.

The magnitude of the surface potential and sign of the surface charge can therefore be controlled with the addition of sodium hydroxide where due to the complexity of the solution chemistry both the surface potential and surface charge density vary as a function of pH. It is therefore possible to manipulate the surface potential and charge sign for both the PCC particles and the marble sculpture surface. Measurement of the surface potential gives the second term required for the determination of the electrostatic energy of interaction, where the third and final term required is the diffuse layer thickness.

### 8.2.2.3.3 Determination of Diffuse Layer Thickness

The potential of the counter ions in the diffuse double layer is predicted to decay approximately exponentially from $\psi_d$ at the stern layer to zero in the bulk solution. The Debye-Hückel parameter $\kappa$ determines the extent of counter ion charge in solution and depends solely on the dissolved calcite ions and hydroxide and sodium ions and not the charged surface. Equation 19, can be used to calculate $\kappa$ where the sum is taken for all ions in solution.

$$\kappa = \left( \frac{\sum \rho_{i} e^{2} z_{i}^{2}}{\varepsilon_{0} \kappa T} \right)^{1/2} m^{-1}$$

Equation 19: Debye-Hückel Parameter$^{171}$

Where $\rho_{i}$ is the number density of ion, in the bulk solution (particles m$^{-3}$)

At a distance $1/\kappa$ from the surface the potential will have fallen to a value $1/e$ of the surface potential and for this reason the reciprocal of $\kappa$ is known as the...
thickness of the diffuse layer or Debye length. The solubility product of calcium carbonate in an aqueous solution of NaOH in contact with air is given in Table 14, and for simplicity, the ions in solution due to dissolved calcite, are taken to be Ca$^{2+}$ and CO$_3^{2-}$ only. This may introduce an error since other ionic species are present in solution however the complex nature of these ions in solution and possible surface complexation species does not allow for determination of all ion concentrations.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$K_{sol}$ / g dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.014</td>
</tr>
<tr>
<td>1 x 10$^{-4}$ M NaOH</td>
<td>0.0087</td>
</tr>
<tr>
<td>1 x 10$^{-3}$ M NaOH</td>
<td>0.0042</td>
</tr>
<tr>
<td>0.01 M NaOH</td>
<td>0.0042</td>
</tr>
</tbody>
</table>

Table 14: Solubility of calcite in varying concentrations of NaOH(open to air)

Table 15, gives the calculated Debye-Huckel parameter, diffuse layer thickness for varying pH and additionally the surface charge density, calculated using Equation 18.
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**Table 15** Results for the Debye-Hückel parameter, diffuse layer thickness and surface charge density for calcite, as a function of calcite solubility and sodium hydroxide concentration

<table>
<thead>
<tr>
<th>pH NaOH</th>
<th>pH NaOH + CaCO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>ζ mV</th>
<th>κ x 10&lt;sup&gt;6&lt;/sup&gt; m&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>1/κ nm</th>
<th>σ&lt;sub&gt;0&lt;/sub&gt; C m&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water only (6.9)</td>
<td>8.06</td>
<td>3.9</td>
<td>77.81</td>
<td>12.9</td>
<td>2.6 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>9.02</td>
<td>-11.9</td>
<td>69.57</td>
<td>14.3</td>
<td>7.3 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>9.73</td>
<td>-16.3</td>
<td>69.59</td>
<td>14.4</td>
<td>9.9 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>10.4</td>
<td>10.5</td>
<td>-18</td>
<td>84.7</td>
<td>11.8</td>
<td>1.3 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>11.3</td>
<td>10.9</td>
<td>-23.3</td>
<td>236.4</td>
<td>4.2</td>
<td>4.1 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>12.4</td>
<td>12.2</td>
<td>-40.2</td>
<td>594.8</td>
<td>1.7</td>
<td>0.018</td>
</tr>
</tbody>
</table>

The results show that the diffuse layer thickness increases by only 1.5 nm between distilled water and a sodium hydroxide solution of pH 10, although the surface charge density increases approximately 4 times over this range. As the pH increases and the concentration of sodium hydroxide greatly exceeds the concentration of dissolved calcite ions (a maximum of ~ 0.03 M NaOH) the double layer is compressed to only 1.7 nm. Therefore the separation distance that can occur between PCC particles at high pH, before electrostatic repulsion occurs, would be expected to be small compared to lower pH solutions.

As observed from Table 15 and the measured zeta potential the surface charge density and surface potential have a tendency to vary as a function of pH and this may have a significant effect when calculating the electrostatic interaction energy as discussed in the following section.

Both parameters for the description of the electrical double layer have been calculated for calcite and Figure 2, shows the influence these parameters have on the EDL both pictorially and graphically, (using the modified flat plate model of Gouy and Chapman).
8.2.2.4 Calculation of $V_R$.

From the above results it is possible to influence both the surface charge and the thickness of the diffuse double layer by adjusting the solubility of calcium.
carbonate in alkaline solutions only. How these diffuse layers interact can be
determined from geometrical approximations using the electrochemical
parameters. It should be noted though that the repulsive force actually arises
due to a decrease in entropy of mixing as two particles approach one another.

8.2.2.4.1 Calculation of $V_R$ for Particle/Particle Interaction

Considering first, the interaction between two PCC particles in the dispersion
medium, typical approximate expressions encountered for $V_R$ as a function of
particle separation ($H$), based on Derjaguin’s method\textsuperscript{173,174}, for the following
boundary conditions are:

\begin{equation}
V_R^\psi = 2\pi\varepsilon_0 \sigma \psi^2_d \ln(1 + \exp[-\kappa H])
\end{equation}

Equation 20: $V_R$ constant potential approximation of Hogg \textit{et al.}\textsuperscript{173}.

\begin{equation}
V_R^\sigma = V_R^\sigma - 2\pi\varepsilon_0 \sigma \psi^2_d \ln(1 - \exp[-2\kappa H])
\end{equation}

Equation 21: $V_R$ constant charge approximation of Weise \textit{et al.}\textsuperscript{174}.

Where these are valid for: potentials below 25 mV, $\kappa a > 1$ and $H \ll a$. The
above two equations can therefore be used for calculating $V_R$ below a solution
pH of 11.5. Above pH 11.5 the surface potential is close to and greater than 25
mV and another approximation, where the Debye-Huckel low potential
approximation is not made, has to be used, Equation 22\textsuperscript{175}

\begin{equation}
V_R = \frac{32\pi\varepsilon_0 \sigma k^2 T^2 \gamma^2}{e^2 z^2} \exp[-\kappa H]
\end{equation}

Equation 22: $V_R$ at high potential (Reemink and Overbeek)

Where

$$\gamma = \frac{\exp[ze \psi_d / 2kT] - 1}{\exp[ze \psi_d / 2kT] + 1}$$
The equation is valid when, \( \exp \left( -\kappa H \right) \ll 1 \), which is observed for the high pH results, and thus can be used to give the approximate repulsive interaction energy for a solution pH 12.4. Since the concentration of NaOH » dissolved CaCO₃ at high pH, the counterion charge number \( z \) is taken to be that of Na⁺.

The two limiting cases of constant potential and constant charge determine how the double layers will interact. The former assumes that as the double layers interact the adsorption of potential determining ions maintains a constant surface potential. The latter boundary conditions assume that as the two layers interact thermodynamic equilibrium with respect to the PDI is not attained and the surface charge remains constant and the potential adjusts (surface potential decreases). In general the interaction profile will lie between the two extremes, where constant surface charge represents the upper interaction energy and constant surface potential the lower interaction energy. Hence both approximations have been used for calculation of the electrostatic interaction energy at solution pH below 12.4.

Israelachvili reports that approximations such as the three above are only accurate for surface separations beyond about one Debye length. Therefore for smaller separations numerical solutions of the spherical Poisson-Boltzmann equation for the two-sphere system are required. Honig and Mul give tables for the exact dimensionless repulsive energy, \( W \), as a function the reduced potential \( Z \) which is equivalent to \( \frac{z e y_0}{\kappa T} \), where the ion charge number has been taken as a weighted average. From these tables of reduced potentials it has been possible to calculate the repulsive energy since \( V_R \) is related to \( W \) through Equation 23, and these interpolated results have been compared to the previous approximations.

\[
W = \frac{V_R}{B}
\]

Equation 23: Honig and Mul relationship
Where:

\[ B = \frac{64 \rho kT}{\kappa} \]

Figure 60 to Figure 63 compare the above approximations for the repulsive energy between two PCC particles as they encounter each other in the electrolyte medium.

**Figure 60: Spherical approximation for \( V_r \) at constant potential**
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Figure 61: Spherical approximation for $V_R$ at constant charge

Figure 62: Hong and Mul exact solution for $V_R$ at constant potential
All four plots give differing results, although the general trend is that with increasing pH, and increasing surface potential the interaction energy increases. However for pH 12.4 where the diffuse layer thickness is small the interaction energy reduces towards zero after a short separation distance.

As expected the values obtained for constant surface charge are greater than the corresponding constant potential although the repulsive interaction extends less with increasing interparticle separation. The Honig and Mul exact solution gives an interaction energy significantly lower than the basic Hogg and Wiese approximations.
8.2.2.4.2 Calculation of $V_R$ for Particle/Surface Interaction

The repulsive interaction between PCC and the marble surface is taken to be the interaction between a spherical particle and flat plate. Again many expressions are based on the Derjaguin approximation. Two approximate analytical expressions for the two limiting cases of constant potential and constant charge have been used, Equation 24 and Equation 25.

$$
V_R = \frac{\varepsilon_0 \sigma}{4} \left[ 2\psi_1 \psi_2 \ln \left( \frac{1 + \exp[-\kappa H]}{1 - \exp[-\kappa H]} \right) - \left( \psi_1^2 \psi_2^2 \right) \ln (1 - \exp[-2\kappa H]) \right]
$$

Equation 24: Sphere-Plate electrostatic interaction – constant potential\(^{173}\)

$$
V_R = \frac{\varepsilon_0 \sigma}{4} \left[ 2\psi_1 \psi_2 \ln \left( \frac{1 + \exp[-\kappa H]}{1 - \exp[-\kappa H]} \right) - \left( \psi_1^2 + \psi_2^2 \right) \ln (1 - \exp[-2\kappa H]) \right]
$$

Equation 25: Sphere-Plate electrostatic interaction – constant charge\(^{174}\).

Both equations are reported to be valid for potentials < 60 mV and $\kappa r > 1$ which covers the range of results in this study\(^ {177}\), however Elimelech and Bhattacharjee\(^ {178}\), have suggested that an over-estimation can arise using the above expressions. No other simple expression exists for mixed geometries and the electrostatic potentials at constant potential and constant charge are plotted in Figure 64 and Figure 65.
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Figure 64: Repulsive interaction energy for Sphere-Plate approximation at constant potential

Figure 65: Repulsive interaction energy for Sphere – plate approximation at constant charge
8.2.2.5 Liftshitz – van der Waals dispersion force contribution to $V_{\text{total}}$

The van der Waals force between the PCC particles and particle/marble surface will tend to be attractive. Three main types of electrodynamic interaction contribute to the van der Waals force:

1. The Keesom force, which is the interaction between two permanent dipoles
2. The Debye force, which is the interaction between one permanent dipole and one induced dipole.
3. The London or Dispersion force which is the interaction between two induced dipoles and exist between all molecules. These arise due to the polarisation of one molecule by fluctuations in the charge distribution in a second molecule, which leads to attraction between the two. The dispersion forces account for nearly all of the van der Waals attraction

Generally the interaction energy varies with the inverse sixth power of the distance for small and intermediate separation distances.

The traditional method of calculation of the van der Waals energy is referred to as the microscopic approach. The interaction is derived from the pairwise addition of the polarizabilities and number densities of the atoms in the two interacting media where this value is referred to as the Hamaker constant. The non-retarded Hamaker dispersion energy, geometrical approximation for two interacting spheres is given by Equation 26.

$$V_A = -\frac{A_H}{6} \left[ \frac{2a^2}{H^2 + 4aH} + \frac{2a^2}{(H + 2a)^2} + \ln \left( 1 - \frac{4a^2}{(H + 2a)^2} \right) \right]$$

Equation 26: Hamaker non-retarded dispersion energy
Where $A_H$ is the Hamaker constant. The Hamaker constant remains the main uncertainty in the calculation of attractive interaction energy by the Hamaker approximation, since it assumes only pairwise summation and neglects the influence of neighbouring atoms, medium and retardation. As a result calculated values can be an order of magnitude incorrect and literature values calculated for calcite in this manner have been avoided. Hamaker constants should be ascertained experimentally or calculated on the basis of Lifshitz theory (which is generally regarded to predict the Hamaker constant to within 10%). The latter has been used here to calculate the Hamaker constant for the studied system.

8.2.2.5.1 Calculation of Hamaker Constant

Modern dispersion force theory (Lifshitz Theory) completely avoids the traditional pairwise summation, since the theory is derived in terms of bulk properties such as dielectric constants and refractive indices. The approach automatically incorporates the effects of neighbouring atoms and the interaction is the result of fluctuations in the electromagnetic field, at certain frequencies, between two particles, modified by the dispersing media. Hence the Hamaker constant can be determined from knowledge of the frequency dependent dielectric properties of the interacting materials and dispersing medium. The full Lifshitz theory involves advanced statistical, mechanical and quantum field theoretical arguments beyond the scope of this work and generally in the colloidal field a number of simplifying expressions are used.

A combination of review papers has been used to determine the van der Waals interaction energy for the systems studied. The first two papers by Hough and White\textsuperscript{180} and Bergstrom\textsuperscript{181} provide the necessary dielectric data for calculating the Hamaker constant for the calcite / water system, Table 16. Whilst the third paper by Bowen and Jenner\textsuperscript{182} reviews and compares simplified methods to exact treatments for calculating the total van der Waals interaction energy.
Considering first the calculation of the approximated Hamaker constant based on Lifshitz theory, two factors need to be taken into consideration for an accurate representation at all separation distances and pH values. These are the effects of retardation and screening due to an electrolyte solution. Both Hough et al. and Bergstrom do not take these factors into consideration for the calculation of the Hamaker constant for calcite in water only, at a short separation distance. The equation for the retarded Hamaker constant for differing interacting media was presented by Horn and Israelachvili \(^{183}\) and is given by Equation 27, where the screening effect developed by Mahanty and Ninham \(^{184}\) is also incorporated, as explained below.

\[
A_{131}(\kappa H) = A_{\xi 0}(1 + 2\kappa H)e^{-2\kappa H} + A_{\xi 21}F(L)
\]

\textit{Equation 27: Screened, retarded Hamaker constant}

The first summation term, \(A_{\xi 0}\), is referred to as the zero-frequency static contribution and includes the Keesom and Debye dipolar contributions that are non-retarded since a permanent dipole exists. \(A_{\xi 0}\) is given by Equation 28.
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\[ A_{\text{res}} = \frac{3}{4} kT \left[ \frac{\varepsilon_n(0) - \varepsilon_a(0)}{\varepsilon_n(0) + \varepsilon_a(0)} \right]^2 \]

Equation 28: Zero-frequency contribution to the Hamaker constant

The second term, \( A_{\xi_2} \), represents the dispersive (London) contribution to the van der Waals interaction energy and can be approximated from the materials dielectric response in the ultra violet region (\( \varepsilon(\omega) \)). \( A_{\xi_2} \) is given by Equation 29

\[
A_{\xi_2} = \frac{3h\sqrt{\omega_2\omega_3}}{128\pi n_0^{7/4}} \frac{X^2n_0 + 2X\Delta n_0\sqrt{n_0} + \Delta n_0^2(3 + 2Y)}{(Y - \sqrt{Y^2 - 1})^{1/2} + (Y + \sqrt{Y^2 - 1})^{1/2}}^{3/4}
\]

Equation 29 Dispersion contribution to calculated Hamaker constants.

where

\[
\bar{n}_0 = \frac{n_1^2 + n_2^2}{2}
\]

\[
\Delta n_0 = n_1^2 - n_2^2
\]

\[
X = \frac{\omega_1}{\omega_3} (n_1^2 - 1) - \frac{\omega_2}{\omega_3} (n_2^2 + 1)
\]

\[
Y = \frac{1}{4\sqrt{\bar{n}_0}} \left[ \frac{\omega_1}{\omega_3} (n_1^2 + 1) + \frac{\omega_2}{\omega_3} (n_2^2 + 1) \right]
\]

Addition of \( A_{\xi_0} \) and \( A_{\xi_2} \) only, gives the non-retarded, non-screened Hamaker constant \( A_{131} \) (where subscript 1 and 3 refer to calcite and water respectively). For the present system this gives a value of \( 1.78 \times 10^{-20} \) J, which is in good agreement with the value calculated by Hough et al. Using Equation 27, the
effects of retardation and screening have been incorporated. Retardation arises due to the finite time of propagation of the electric field which for increasing particle separation can become comparable to the period of the fluctuating dipole itself. The returning induced electric field finds that the direction of the instantaneous dipole of the first particle is different resulting in a decreased attractive interaction. Thus, with increasing separation the dispersion energy decays faster than the inverse sixth power, and is known as the retardation effect which is described by Equation 30

\[ F(L) = \left[ 1 + \left( \frac{\pi L}{4 \sqrt{2}} \right)^{\frac{3}{2}} \right]^{2/3} \]

Equation 30: Retardation factor for calculation of Hamaker constants

Where:

\[ L = n_0 \left( n^2 - n_0^2 \right)^{\frac{1}{2}} \frac{H \sqrt{\omega_1 \omega_3}}{c} \]

Screening occurs when free ions in solution cause the electromagnetic fields to become screened due to polarisation of these charges. Only the zero frequency contribution is screened not the dispersion electromagnetic field, which due to its high frequency means the electrolyte ions can not respond and hence are not polarised. A screened electric field decays approximately exponentially with distance according to \( e^{-2xH} \). Since both propagating and reflected fields are screened during the interaction the net effect is that the zero frequency term is reduced by a factor proportional to \( e^{-2xH} \).

From Equation 27, the screened, retarded Hamaker constant as a function of separation distance for each calcite / pH solution has been calculated and it is assumed to be the same for both PCC and PIM, Figure 66.
8.2.2.5.2 Calculation of $V_A$ for Particle/Particle Interaction

In terms of the full expression for calculation of the van der Waals interaction energy, Bowen et al.\cite{182}, point to two approximations that compare favourably to the exact results of Gorner and Pich\cite{185}, for two interacting spherical particles. These two approximations are the non-retarded Hamaker geometrical approximation using the screened, retarded Hamaker constant and Vincents short range retarded approximation again using the screened, retarded Hamaker constant, Equation 26 and Equation 31 respectively.

Figure 66: Calculated Hamaker constant for calcite / pH solution as a function of separation distance
For small separations below 5 - 7 nm the Vincent approximation was found to be comparable to the exact results although the Hamaker approximation was superior over the total interparticle separation range. Hence both approximations have been compared for the interaction between two PCC particles and Figure 67 and Figure 68 give the reduced van der Waals energy in terms of thermal energy $kT$ for the Vincent approximation and Hamaker approximation respectively.

---

**Figure 67:** Vincent spherical approximation for dispersion energy as a function of pH.
It is generally accepted that the interaction energy becomes insignificant compared to the thermal energy of the particles when $\frac{V_A}{A_{131}}$ is less than about 0.1. From the results for the interaction between two PCC particles this is observed to be at a particle separation beyond 10-15 nm. Hence only when the particles approach closer than this limit do they experience a significant attractive interaction. Since deviations as large as 30% for 100 nm particles have been observed between the Hamaker approximation and the Vincent approximation below 7nm, the latter approximation is most accurate.

**8.2.2.5.3 Calculation of $V_A$ for Particle/Surface Interaction**

For the calculation of the van der Waals interaction energy between a PCC particle and the marble surface, Equation 32, for a sphere / plate geometry utilising the screened, retarded Hamaker constant calculated previously, has been employed.
Figure 69, plots the van der Waals interaction for the varying pH solutions as a function of the thermal energy. Compared to the interaction between two spherical particles, it is observed that the attractive influence extends further where the ratio of 0.1 for $V_A/A_{131}$ is found typically to fall between 30 – 35 nm.
8.2.3 Total Energy of Interaction with Comparison to Experimental Observation

8.2.3.1 $V_T$ Energy Profiles for Particle/Particle Interaction

As outlined previously the total energy of interaction is the sum of the electrostatic energy ($V_R$) and the dispersion energy ($V_A$). The above two sections have determined both contributions to the interaction energy between colloidal particles and between colloidal particle and marble surface. Various approximations have been used, to study their limitations and find a convenient approximation for the future study of such systems. In order to determine the effectiveness of these predictive models the total interaction profile for PCC particles has been compared to experimental observation of the colloidal stability, discussed in the following section.

For the total interaction between the colloidal particles manipulation of the surface charge and solution chemistry was to try and produce a stable or flocculated (weakly aggregated) suspension, such that the particles did not form an aggregate larger than 1/3 of the pore diameter. Figure 70 to Figure 75, give the total energy of interaction as a function of the thermal energy $kT$, for each pH, where for each pH the various approximations are compared.
Figure 70: Total energy of interaction for PCC in water - comparison of approximations

Figure 71: Total energy of interaction for PCC at pH 9 – comparison of approximations
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Figure 72: Total energy of interaction for PCC at pH 10 – comparison of approximations

Figure 73: Total energy of interaction of PCC at pH 10.4 – comparison of approximations
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Figure 74: Total energy of interaction for PCC at pH 11.3 – comparison of approximations.

Figure 75: Total energy of interaction for PCC at pH 12.4 – comparison of approximations.
The resulting interaction profiles suggest a number of conclusions that are summarised below:

1. The interaction profiles where the Honig and Mul interpolated tables have been used, give consistently lower potential energies at both constant charge and constant potential to the corresponding Hogg approximations at constant charge and potential. The reason for using the Honig and Mul interpolated tables was to try and give a more accurate interaction profile below a separation distance of one Debye length. This diffuse layer thickness is typically between 12-15 nm for a pH range between 8 - 10.5 and less than 4.5 nm above pH 11. From the above plots this suggests that PCC dispersed in water (∼ pH 8.1) is unstable resulting in aggregation into a primary minimum. With increasing pH a small potential energy barrier to coagulation also increases between 5 –10 nm separation where this is approximately $\frac{1}{2} kT$ at pH 9, 1-2 $kT$ up to pH 10.5 and 4.5 $kT$ at pH 11.3. At pH 12.4, the interpolated tables for $V_R$ were only available for a short separation distance due to the thin diffuse layer thickness. However the results indicate that at separations below 10 nm the PCC particles will coagulate. As such slow coagulation may be expected to occur. Honig and Mull suggest that in the presence of a mixed electrolyte the tables break down and whilst weighted averages were taken for the charge number the interaction profile may deviate from experimental results.

2. The Hogg and Wiese approximations result in much higher potential energy barriers to coagulation, with the latter, constant charge approximation, appearing to give unrealistically high values in order of $kT$. It may be presumed that as the two particles approach and the double layer is compressed the potential is kept approximately constant by the adsorption of potential determining ions (increase in surface charge). Hence the true value will most probably lie closer to the constant potential results and the constant charge predictive models can be neglected.
3. Considering the Hogg constant potential profiles. For PCC dispersed in water it is predicted, in line with that observed for the Honig and Mul approximations, that the suspension is unstable resulting in coagulation. With increasing ionic strength (and increasing surface potential $\psi_0$) a potential barrier to coagulation arises around 5 nm particle separation and is in the order of $3 - 8 kT$ between pH 9 - 11.3. The energy profile after the peak maximum decays slowly with distance and would predict that the colloid would be stable. At pH 12.4, the energy barrier to coagulation is large, although a secondary minimum is observed and flocculation is predicted.

4. The use of either the Hamaker or Vincent approximation for $V_A$ result in very similar energy profiles when added to $V_R$. Deviations only begin to occur below 10 nm separation as predicted by Bowen, however the maximum deviation is in the order of 10% and either approximation could be used for the predictive model.

These results have been compared to simple experimental observation of PCC stability over time.

8.2.3.2 Observed PCC stability

PCC was dispersed in the aqueous medium either by ultrasonically shaking or by shaking by hand, to study the effect of aggregate size on stability. Once dispersed the volume of PCC solution from clear solution was determined as a function of time, giving an indication of sedimentation rate, Figure 76.
As observed from the results minimal agitation resulted in rapid sedimentation and is assumed to be an effect of aggregate size, where minimal electrostatic stabilisation occurs. In comparison, when the aggregate size is reduced towards one particle by ultrasonic shaking, the sedimentation rate drops. Noticeably slow aggregation is observed and the colloidal dispersion for all pH solutions are not stable which at first would appear to contradict the total energy of interaction plotted in the previous section. However, from observation of the equilibrated volume it is observed that the all samples flocculate in a secondary minimum rather than coagulate into a deep primary minimum, Figure 77 and Figure 78.

Figure 76: Sedimentation volume of PCC as a function of time.
Figure 77: Sedimentation volume of PCC dispersed by ultrasonic shaking as a function of time and pH, where samples exhibit flocculation.
Therefore an energy barrier to coagulation does exist and the solutions are stable with respect to the primary minimum, forming weakly held aggregates that can be readily reversed. This can be compared to initial results obtained for a non-aqueous polar medium as the dispersing agent, where the dispersion was observed to be electrostatically stabilised, Figure 79. With time the colloid enters a deep primary minimum where the sedimentation volume is compact compared to Figure 77 and is difficult to re-disperse.

No other characterisation of the methanol systems has been conducted and further work in this area of non-aqueous solvents would be interesting. It is
postulated that the reduced polarity of the medium reduces the solubility of calcite such that a thick diffuse double layer forms increasing $V_R$.

From these observations the predictive model using the Hogg-Vincent approximations for constant potential give the closest match to the observed results with respect to the presence of an energy barrier to coagulation. None of the models predicted a secondary minimum except at pH 12.44, and hence at larger interparticle separations the models break down. For determination of $V_R$ the equations become invalid as $H \to a$, and may account for some overestimation. Secondly the complexity of ions present in solution makes accurate determination of the diffuse layer thickness impossible and introduces another sources of error. Although the models fall short of predicting the secondary minimum the fact that the PCC particles flocculate is a good result in terms of consolidation. The particles are only aggregated by weak attractive forces, hence the voluminous sediment, and provided they can be re-dispersed on application they are readily reversible into individual particles. This has been achieved by the use of a bottom loading airbrush, where the particles can be deposited onto the surface in small droplets.

8.2.3.3 $V_T$ Energy Profiles for PCC/Marble Surface Interaction.

The calculated total energy of interaction as a function of separation distance for the PCC particle interacting with the marble surface for each pH solution are shown in Figure 80 to Figure 85.
Figure 80: Sphere-plate total energy of interaction in water

Figure 81: Sphere plate total energy of interaction at pH 9
Figure 82: Sphere-plate total energy of interaction at pH 10

Figure 83: Sphere-plate total energy of interaction at pH 10.5
Figure 84: Sphere - plate total energy of interaction at pH 11.3

Figure 85: Sphere - plate total energy of interaction at pH 12.4
Although the interaction profile predicts that at small separations the particle will be attracted to the surface, at a pH below 11.3 this attractive energy does not penetrate more than half a particle radius. At greater interparticle distances there appears to be minimal electrostatic interaction, assuming that the approximation is relatively accurate. This means that there would be no tendency for particles to repel or attract to the surface and thermal energy and hydrodynamic properties only influence particles. A large repulsive energy would not be ideal since the particles will have no tendency to adhere to the pore walls or penetrate the pore entrance, whereas a small repulsive energy would prevent excessive accumulation at the surface since the particles should penetrate the surface. So although at short separation distances the interaction is attractive no interaction at larger separation distances represents an ideal set of conditions for penetration into the sample. Some material will naturally accumulate on the surface but also material will penetrate into the porous network and adhere to the surface by electrostatic interaction.

From the above results it is suggested that a pH around 10.5 be used for the consolidation procedure. This ensures all surfaces are negatively charged, but that the surface potential and ionic concentration is not too large, hence minimal foreign material is introduced ($\sim 10^4$ M). PCC once fully dispersed remains stable for at least one hour and any aggregates that sediment out are only held in a weak secondary minimum and are easily re-dispersed.

To test the effectiveness of the method for penetrating the surface rather than forming surface crusts, small samples were sprayed with the solutions and analysed by mercury porosimetry, Table 17.
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Table 17: Comparison of pore distributions from mercury porosimetry results for various treatments as compared to non-treated weathered and non-weathered marble samples

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Pore distribution range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 - 10 μm</td>
</tr>
<tr>
<td></td>
<td>% of total distribution</td>
</tr>
<tr>
<td>Non-weathered</td>
<td>33% 60 μm 8% 4 μm 59% 0.017 μm</td>
</tr>
<tr>
<td>untreated</td>
<td>58% 58.2 μm 16% 3.25 μm 26% 0.024 μm</td>
</tr>
<tr>
<td>Ca(OH)₂ 20 apps</td>
<td>55% 49 μm 29% 4.5 μm 16% 0.03 μm</td>
</tr>
<tr>
<td>PCC 11 apps</td>
<td>38% 32.4 μm 30% 3.9 μm 32% 0.032 μm</td>
</tr>
<tr>
<td>PCC 8 apps</td>
<td>28% 44 μm 28% 4.5 μm 44% 0.014 μm</td>
</tr>
<tr>
<td>Ca(OH)₂ 6 apps</td>
<td></td>
</tr>
</tbody>
</table>

The total porosity is not compared between samples since the fragments were not from exactly the same source and as observed from previous results where the sample appears to be weathered to a similar extent the actual porosity can be significantly different. All samples though were highly friable and after treatment a porosity around 20% was observed for most samples. Ideally, a large fragment that is severely weathered and that can be sub-divided into smaller samples is required to determine overall porosity reduction. From the above table some conclusions can be drawn from studying the change in pore size distribution. As observed from section 5.3.1, as a sample weathers the pore distribution generally follows the same trend irrespective of overall porosity with a trimodal distribution. The mid-range of pore sizes and largest pore size range increase in contribution to the total porosity. Whilst the smallest pore sizes attributed to interstitial spaces in the crystal lattice decreases in
contribution to total porosity. It would be expected that if the applied material penetrates the surface the % pore distribution should shift back towards the smallest pore distribution range.

Many applications of calcium hydroxide alone result in the smallest range of pores contributing less to the overall porosity and this reduction is attributed to the solution penetrating to these regions. Additionally, the increase in % contribution to total porosity of the mid range of pores is attributed to the reduction in the large pore size distribution by partial filling thus effectively producing smaller pore sizes.

If only calcium carbonate is used as a consolidant the smaller pore sizes cannot be accessed by the particles due to the particle diameter (0.11 µm) being larger than the pore diameter. Hence the particles can only partially fill the large and mid-ranged pore sizes and a corresponding shift in % porosity contribution towards the lowest pore size range is observed.

Combining both procedures by first applying the PCC followed by the hydroxide solution, sees the pore distribution shift such that the smallest pore sizes contribute most to the overall porosity. Therefore the other pore size ranges must be partially filled and hence PCC particles must be penetrating the surface.

PCC and calcium hydroxide solutions are used in tandem for two reasons. Firstly the PCC acts to partially bulk fill the larger pores and channels more efficiently than would be achieved using hydroxide solutions alone. Once partially filled the particles need to be interlinked to form a cohesive network. The nucleation and growth of calcium carbonate directly from a calcium hydroxide solution is used as the binding agent between particles and between particle and pore wall, where nucleation causes the crystals to bond and grow into one another. Figure 86, is an SEM image of the resulting network of applied PCC and nucleated calcium carbonate.
Finally the overall consolidation procedure was tested on various areas on the highly friable base of the second century Roman sculpture, using the charge stabilised PCC dispersion (5% w/v) at pH 10.5 and a clear solution of calcium hydroxide. The base area on the sculpture has minimal crystal cohesion and the slightest touch results in significant loss of material. Initial trials were carried out on small areas to test the effectiveness of the procedure and look for any adverse effects. Figure 87, is a photograph of these areas after treatment.
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Figure 87: Photograph of treated areas on the base of the 2nd century Roman sculpture.

Area 1, was consolidated with six applications of PCC using the bottom loading airbrush, where a distance of greater than 5 cm is required for the first few applications to prevent excessive loss of material. No surface crust formed and whilst the area became firmer to the touch some material was still lost. Area 2, was consolidated with a 1% w/v acetone solution of Paraloid b44, which was pipetted onto the surface. This resulted in consolidation of the area with no loss of material. Area 3, was treated with calcium hydroxide only and after 6 treatments the surface was still friable but felt slightly firmer to the touch than an unconsolidated area. Area 4, was the control and was sprayed with distilled water only, 6 times. Once dry the surface remained unconsolidated. Areas 5 and 6 were treated identically with six applications of calcium hydroxide followed by six applications of PCC and finally six further applications of calcium hydroxide. Once dry no surface crust or other external visible changes to the friable marble was observed. The area was consolidated and was firm to the touch with no significant loss of material.

No adverse side effects were observed on these small areas and a larger area on the right hand side of the base was treated under the same conditions as for
areas 5 and 6. Each application was applied such that the surface never became saturated hence preventing surface crust formation, Figure 88

![Figure 88](image.png)

Figure 88: Photograph of larger areas treated on the 2nd century Roman sculpture using the combined PCC and Ca(OH)₂ procedure.

It was found that the side treated with the combination of calcium hydroxide solutions and electrostatically stabilised PCC solutions produced a surface that was firm to the touch with no loss of material. In comparison the opposite side was highly friable where the lightest touch resulted in the loss of many grains of calcite.

8.3 Consolidation Procedure Summary

A consolidation procedure has been developed for highly friable areas like those characterised from the Ince Blundell collection. DRIFT spectroscopy and XPS surface characterisation techniques as well as SEM and mercury porosimetry have studied these areas. The highly friable regions are comprised predominantly of calcite where the porosity is greater than 30% with the mid
range and largest range of pore sizes contributing most to the overall porosity. These areas require stabilisation to prevent complete degradation of the existing material.

Development of a consolidation procedure has been based on the modification of existing inorganic methods focusing on the physical chemistry and surface interaction between consolidant and marble.

The reintroduction of calcium carbonate into the marble fabric represents the most sympathetic procedure, with the least amount of foreign material introduced to the system and issues such as salt cycles and thermal expansion coefficients avoided. Traditional lime methods have been shown to be inefficient for the total consolidation of the Ince Blundell collection due to its low solubility, typically 55 applications would have to be applied to produce a 5% reduction in porosity. Traditionally the hydroxide solutions are carbonated by atmospheric CO₂, which may leave solid Ca(OH)₂ in the pore network where carbonation is incomplete. Under an atmosphere of CO₂(g), it is possible to nucleate and grow calcium carbonate crystals directly from solution onto the marble surface, where there is some evidence of orientated crystal growth. However, an additional method of reintroduction of calcium carbonate is required to reduce the number of applications of hydroxide solutions. The direct deposition of calcium carbonate particles into the pore network has been investigated.

A number of factors have to be considered to prevent the applied particles becoming little more than a paste or poultice where surface crust formations would occur. Hence the particle size in relation to pore size was the first consideration. Synthetically precipitated calcite generally gives a smaller particle size than powdered marble, and was observed to be most likely to penetrate the mid-range of pore sizes. However the dispersed particles may have a tendency to aggregate in solution effectively increasing the diameter of the particles such that application to the surface results in crust formation. These interactions are defined by the DLVO theory and manipulation of the
surface chemistry can change the electrostatic interaction minimising the tendency for aggregate formation and particle/marble surface interaction. Electrostatic manipulation was studied by measurement of the surface charge (zeta potential) as a function of pH and estimation of the diffuse double layer thickness. These two parameters allowed approximate calculation of the electrostatic repulsion interaction energy. The van der Waals attractive energy was approximated using the Hamaker constant which was accurately determined allowing for retardation and screening effects due to the electrolyte concentration. The total energy of interaction predicted a barrier to coagulation but did not predict flocculation into the secondary minimum, which was observed for all samples. The flocculated PCC solutions were voluminous and are only held together by weak attractive forces, such that minimal energy is required for re-dispersion. Application to the marble surface was best achieved using a bottom loading airbrush, which acted to break up any aggregates.

A solution pH of ~ 10.5 was determined to provide the best conditions for deposition of PCC into the pore network and mercury porosimetry pore distribution results indicate that the pores do become partially filled.

The overall procedure is to apply PCC to a highly friable area to bulk reduce the porosity by deposition into the porous network and then to use the calcium hydroxide solutions under an atmosphere of CO$_2$ to nucleate and grow calcium carbonate that links these particles together. Thus forming a rigid but open network. Application to the highly friable areas on the 2nd Century Roman sculpture appear promising with the areas treated becoming firm to the touch with minimal loss of calcite crystals and no detrimental visual effects.
Chapter 9 WEATHERING PROTECTION USING MONOLAYER COATINGS

9.1 Introduction

The proposed consolidation method will not prevent further chemical weathering from acidic gases such as sulphur dioxide, since only calcium carbonate is introduced into the existing material. As such if at this stage of conservation an object was to be placed back into the environment, with a freshly cleaned surface, the rate of deterioration would continue as before and may even be accelerated. It has therefore been necessary to consider the development of a protecting layer that could be used in conjunction with the proposed consolidation.

The whole ethos of this research has been to be as sympathetic to the original marble as possible, such that only the necessary amount of material is applied and that this material is compatible to the original. However, a weathering protection layer means that a foreign compound has to be introduced. This section has therefore been approached with the aim to only apply coatings in the order of molecular dimensions. This keeps the applied compound to a minimum, such that there is no pore filling, no effects from differences in thermal expansion, and no change in the aesthetic of the original material.

The first step was to study the adsorption of the potentially protective coatings by modelling the process on powdered Italian marble (PIM) where analysis by DRIFT and XPS was used to determine adsorption and the thickness of the layer.

The non-coated and coated PIM samples were then exposed to a polluted environment under extreme conditions to test whether the coatings inhibit the chemical weathering mechanism. Since calcium sulphate dihydrate is the main alteration product observed on the Ince collection, sulphur dioxide interaction with marble was studied. Research was conducted under accelerated, dry deposition conditions, since inconsistency still exists in the literature for the
mechanism of reaction, whereas the wet deposition mechanism by acid rain is generally accepted\textsuperscript{37}. As discussed in the experimental section a specifically designed exposure rig that allows careful control of the relative humidity was used and the model system of powdered Italian marble (PIM) studied over a range of relative humidity. The effects of the coatings on the PIM were then assessed under the same conditions and the resulting weathering mechanisms compared to the non-coated PIM.

9.2 Characterisation of Monomolecular Coatings on PIM.

9.2.1 Calcium Stearate Formation
Calcium stearate was studied in more depth than the other two coatings, since its use on industrial fillers in the plastics industry is well documented\textsuperscript{187,188}. In this industry the formation of calcium stearate is used as a coating, to reduce the surface energy of the filler such that it disperses with the polymer. In terms of use for weathering protection, the adsorption of a layer (with a thickness of the order of molecular dimensions) onto the surface of calcium carbonate is to reduce the surface energy such that the surface becomes less likely to physisorb water, i.e. is hydrophobic, Table 18.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Energy mJ m(^{-2})</th>
</tr>
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<tbody>
<tr>
<td>Calcite</td>
<td>65-70</td>
</tr>
<tr>
<td>Stearate coated calcium carbonate</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 18: Surface energy of coated and non-coated calcium carbonate\textsuperscript{188}.

For protection it is vital that the applied stearate fully covers the surface of calcite, if the stearate is adsorbed in patches the weathering mechanisms will still occur. Consideration has therefore been given to the chain conformation once the stearate has adsorbed onto the surface by studying three levels of
coating: 0.55%, 1.1% and 2.2% stearate on PIM by weight (w/w). The percent weight of sodium stearate used was specifically determined to produce a coating in the order of one monomolecular layer. This was calculated from knowledge of the surface area of the model material and the area occupied by one stearate molecule on that surface, assuming the ‘brush’ type model and access to all reactive sites, Figure 89. In the ‘brush model’, stearate molecules are assumed to pack tightly together with the chain vertical and the polar head group only, occupying an area on the surface of $20 \times 10^{-20} \text{m}^2$. According to this model, 1.1% w/w of sodium stearate should theoretically represent a monolayer coverage.

![Brush Model](image)

Figure 89: Surface coverage of stearate molecule according to brush model

This model may give an over-estimation of the required level of sodium stearate to completely cover the surface since at the other extreme the stearate alkyl chain could be assumed to lie parallel to the calcite surface, Figure 90. If this occurs the area on the calcite surface occupied by one stearate molecule increases by a factor of 5.6 and hence the concentration of sodium stearate required to fully cover the surface decreases. Hence coating the PIM at three
levels. The aim was to try and keep the applied foreign material as low as possible, and if the chain conformation varies due to the overall concentration, applied testing, with the $SO_2(g)$ rig, of the three coating levels will indicate whether the surface is fully covered.

\[ \text{Layer Model: Area occupied on the surface is } 114 \times 10^{-20} \text{ m}^2 \]

\[ \text{Figure 90: Surface coverage by a stearate molecule according to the layer model} \]

The coating efficiency and thickness of the adsorbed layer has been determined for each weight % by DRIFT spectroscopy and XPS respectively.

9.2.1.1 DRIFT Results

Samples were removed from the coating reaction every five minutes for the 1.1% w/w coverage, washed thoroughly, dried and analysed by DRIFT spectroscopy. An alkyl absorption is observed in the 3000 - 2800 cm$^{-1}$ region and is partially obscured by the calcium carbonate first overtone $V_3$ vibration of the crystal lattice, Figure 91.
Figure 91: DRIFT spectra of obscured alkyl absorption

The alkyl absorption is attributed to the C-H vibration of the stearate chain and can be further resolved by subtraction of the non-coated PIM from each of the coated spectra. Spectral subtraction reveals three sharp peaks at 2958 cm\(^{-1}\), 2916 cm\(^{-1}\) and 2849 cm\(^{-1}\), where the intensity of each peak differs, Figure 92. These peaks can be attributed to the asymmetric and symmetric stretching of the CH\(_2\) group. Additionally, a stearate peak is observed at 1578 cm\(^{-1}\) and is indicative of calcium stearate, this is not assigned to sodium stearate since the XPS spectra found no sodium present, as reported in the next section. A small broad band is present at 1740 cm\(^{-1}\) and may indicate the presence of some residual stearic acid, although the size of the normally intense carbonyl stretch is very small compared to the calcium stearate stretch at 1578 cm\(^{-1}\) and the concentration must be minimal, Figure 93.
Figure 92: Resolved DRIFT spectra of alkyl region of adsorbed stearate molecule on PIM

Figure 93: Resultant DRIFT Spectra after PIM Subtraction from Coated Sample
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The small OH band observed on the PIM coated samples at 3080 – 3350 cm\(^{-1}\) cannot be completely attributed to the presence of any residual acid groups since the peak at 1750 cm\(^{-1}\) is so small. It could be attributed to water chemisorbed in the crystal lattice, which becomes visible after adsorption of the stearate molecule displaces the layers of hydrogen bonded (physisorbed) water. In the FTIR technique physisorbed water can cause a broadening of peaks in this region, which with increased hydrogen bonding are no longer detected, even though physisorbed water is known to exist on many surfaces.

The ratio of the integrated peak between 2770 – 3050 cm\(^{-1}\), incorporating the \(v_3\) overtone band and alkyl stretching vibration and the integrated combination band of the calcite crystal between 2400 – 2600 cm\(^{-1}\) has been plotted for each extraction time, Figure 94. This gives a direct measure of the concentration of coating adsorbed over the reaction period. Noticeably the coating concentration is constant at all reaction times suggesting that the adsorption of stearate to form calcium stearate is highly favourable for the natural calcite (PIM), an important characteristic for coating marble surfaces.

![Figure 94: Plot of peak ratio against reaction time to follow concentration of adsorb adsorbed stearate on PIM](image)

- 200 -
Since the consolidation procedure uses the smaller particle size of the precipitated calcite, adsorption was also studied to observe any potential differences between the natural calcite and synthetic calcite. The adsorption of the sodium stearate onto precipitated calcium carbonate (PCC) to give a theoretical one monomolecular coating was studied as a function of reaction time, Figure 95 and the peak ratio is plotted in Figure 96.
Figure 96: Plot of peak ratio against reaction time to follow concentration of adsorbed stearate on PCC.

A similar trend to PIM is observed for the formation of calcium stearate on the surface and no OH band is observed around 3200 cm\(^{-1}\), however it is observed that the peak ratio is larger compared to the natural calcite. This is can be attributed to the difference in size of the two powdered samples.

The 0.55% and 2.2% w/w coating levels were reacted for 30 minutes at 80°C and were also analysed by DRIFT spectroscopy and compared to the 30min 0.11% w/w coated PIM. Subtraction of the non-coated PIM spectra from the coated spectra, reveals that the alkyl concentration increases with increase in % weight of coating, Figure 97. Again, there is an OH absorption observed for the coated PIM.
9.2.1.2 XPS Analysis of Stearate Coated PIM

XPS analysis was used to determine the thickness of the adsorbed coatings and the elemental composition on the surface, after 30 minutes reaction.

From the broad scan spectra no residual sodium is detected by XPS, which is more surface specific than DRIFT, analysing the outer few nanometers of the surface and detecting elements down to < 1 atom %, Figure 98
Figure 98: XPS broad scan spectra of non-coated and stearate coated PIM

Figure 99, shows the atomic percent concentration, %[atom], as a function of the stearate concentration as determined from the broad scan spectra. As expected, it is observed that the atomic carbon increases with added stearate whilst both the calcium and oxygen elemental composition decreases due to attenuation of photoelectrons in the adsorbed layer.
To determine the thickness of the adsorbed layer it is important that the carbon due to the calcite substrate can be accurately differentiated from the carbon due to the organic overlayer. This is achieved due to the susceptibility of the elements to their chemical environment that manifests as slight differences in the kinetic energy of the emitted photoelectrons. The carbon due to the stearate alkyl chain is found to differ from the carbon due to calcite by up to 4.9 eV.

Table 19

<table>
<thead>
<tr>
<th>% weight coating</th>
<th>C 1s</th>
<th>O 1s</th>
<th>Ca 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>284.6, 288.6</td>
<td>530.5</td>
<td>346.3</td>
</tr>
<tr>
<td>0.55</td>
<td>284.6, 289.1</td>
<td>531</td>
<td>346.8</td>
</tr>
<tr>
<td>1.1</td>
<td>284.6, 289.5</td>
<td>531.5</td>
<td>347.3</td>
</tr>
<tr>
<td>2.2</td>
<td>284.6, 289.5</td>
<td>531.4</td>
<td>347</td>
</tr>
</tbody>
</table>

Table 19: Elemental binding energies of non-coated and stearate coated PIM
All the binding energies are seen to increase as the calcite forms a calcium stearate layer and this is attributed to differential charging effects between non-coated and coated surfaces 190,191.

High resolution C 1s spectra were curve fitted and measurement of the relative intensity of the these peaks were used for the determination of layer thickness. Peak fitted, high resolution C1s spectra for the 0.55%, 1.1% and 2.2% w/w of coating are shown in Figure 100, Figure 101, and Figure 102 respectively.

There are two types of chemical environment associated with the stearate molecule, the alkyl chain, and the carbon at the carboxylate polar head group, where the intensity ratio should be 17:1 respectively. This difference in chemical environment gives rise to a shift in binding energy of ~3 eV 192 and both peaks have been fitted. The measured ratio is observed to be 14:1, which is in reasonable agreement given the low intensity of the peak and the inevitable ambiguity in selecting an accurate baseline.

---

**Figure 100:** Curve fitted high resolution C1s XPS spectra of 0.55% w/w stearate coated PIM
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Figure 101: Curve fitted high resolution C1s XPS spectra of 1 1% w/w stearate coated PIM

Figure 102: Curve fitted high resolution C1s XPS spectra of 2 2% w/w stearate coated PIM
As can be seen from the spectra, PIM covered with 0.55% w/w of stearate has a larger C1s contribution from the carbonate carbon than the coating carbon as opposed to the other two spectra where the reverse is observed. This is related to the thickness of the layer, the thicker the layer the more attenuated the photoelectrons emitted from the calcite substrate. The attenuation of photoelectrons therefore allows estimation of the overlayer thickness.

The coating thickness on the PIM is estimated from the ratio of the total relative intensity of the high energy C 1s photoelectron peaks due to coating (I_{coat}) and carbonate substrate (I_{sub}). These values are compared to a spherical thickness model which allows for the powder geometry and which takes account of the coating on the attenuation of photoelectrons emitted from the substrate (calcite), Equation 33. The main limitation of the equation is that it assumes uniform coating thickness.

$$I_{coat} - \frac{n_c \lambda_c}{I_{sub} n_s \lambda_s} \int_0^{\pi/2} \cos \theta \sin \theta \left(1 - \exp \left[-\frac{d}{\lambda_c \sin \theta}\right]\right) d\theta$$

**Equation 33: Calculation for the thickness of adsorbed coatings**

Where $\lambda_c = 4.5$ nm and $\lambda_s = 2.67$ nm which are the attenuation lengths for the C 1s photoelectron in the stearate and inorganic substrate respectively. The number density of carbon atoms present in the coating and the substrate are represented by $n_c$ and $n_s$ respectively and are calculated from the density of octadecene and calcium carbonate. $d$, is the thickness of the layer (nm).

Using the above constants it is possible to estimate the variation in XPS intensity ratio ($I_{coat}/I_{sub}$) on increasing thickness and the results are plotted in Figure 103.
The ratio of the relative intensities of $I_{\text{coated}}$ and $I_{\text{substrate}}$ of the stearate coated samples, determined from the peak fit of the high resolution C1s spectra have been compared to the spherical model and the layer thickness calculated, Table 20.

<table>
<thead>
<tr>
<th>% weight of coating</th>
<th>$I_c/I_s$</th>
<th>Thickness of coating / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>0.75</td>
<td>0.5-0.6</td>
</tr>
<tr>
<td>1.1</td>
<td>1.78</td>
<td>1.1-1.2</td>
</tr>
<tr>
<td>2.2</td>
<td>2.17</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 20: Thickness of stearate coating on PIM for varying levels of applied sodium stearate
XPS analysis has allowed determination of the thickness of the adsorbed layer as a function of % w/w of sodium stearate used to coat the PIM. The maximum theoretical thickness according to the brush model is 2.4 nm and from the observed results the coating conformation lies somewhere between the 'layer' and 'brush' models. Research on PCC fillers have suggested that the maximum thickness obtainable is actually controlled by the number adsorption sites per unit area on the calcium carbonate surface. For stearate on PCC a monolayer coating thickness of 1.3 nm has been reported\textsuperscript{187,195}. The small increase in peak area for adsorbed stearate as measured by DRIFT spectroscopy and the small increase in thickness of the adsorbed layer between 1.1% and 2.2% w/w of sodium stearate suggests the maximum concentration of sodium stearate for coating the marble surface must be nearly attained. Therefore the maximum thickness must be approximately 1.4 nm for coating on PIM and this represents a monolayer coverage. At 0.55% w/w of sodium stearate the thickness of the coating is approximately half 1.1% w/w and it is suggested that the number of stearate molecules is less than the number of binding sites on the surface and so the chains lie flatter on the surface. In terms of complete coverage of the surface neither XPS nor DRIFT can determine whether patches of calcium carbonate are exposed. However research using a combination of XPS and BET has shown the surface of PCC to be fully covered at approximately 0.66% w/w of added sodium stearate\textsuperscript{196}. As such the lowest coating level used in this study may not be fully covering the surface of the marble.
9.2.2 DRIFT and XPS Analysis of Other Coatings on PIM

PIM coating was also attempted with two other compounds:

1. Poly(ethylene acrylic acid) co-polymer (PEAA) \( \text{CH}_3(\text{CH}_2)_m(\text{CH}_2\text{COOH})_n \), which will give a much thicker layer and act as a physical barrier to gas and water adsorption.

2. Oxalic acid \((\text{COOH})_2\), a natural degradation product observed on most surfaces in varying concentrations, it does not have a low surface energy and will still allow water adsorption.

9.2.2.1 DRIFT Results for PEAA and Oxalic Acid

Molecular weight determination of the PEAA copolymer by Gel permeation chromatography (GPC) gave an average value of 6500 g mol\(^{-1}\) and from manufacturer details it was calculated that approximately 10% is due to the acrylic acid. Pre-determination of the number of these groups binding to the calcite surface was impossible and an underestimate of surface area coverage \((60 \times 10^{-20} \text{ m}^2)\) i.e. excess of the polymer was used to coat the PIM (9% w/w).

DRIFT analysis of the coated PIM, shows that the polymer has adsorbed onto the surface due to the presence of the large alkyl absorption between 2920 – 2850 cm\(^{-1}\) and the low intensity absorption at 1565 cm\(^{-1}\) and 1396 cm\(^{-1}\) which are indicative of acid salts, Figure 104. Additionally the resolved spectrum reveals the presence of a comparably intense carbonyl band at 1694 cm\(^{-1}\) indicative of intramolecular hydrogen bonded acid groups\(^{197}\), attributed to the non surface bonded carboxylic acid groups in the polymer coil, Figure 105.
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Figure 104: Comparison of PEAA coated PIM to non-coated PIM and ATR-FTIR spectra of PEAA

Figure 105: Resolved spectra of PEAA coated PIM
Calcium oxalate is found on many marble surfaces and where the thickness of this layer is large, it is believed to prevent weathering mechanisms. Matteini et al. who have artificially produced oxalate layers in excess 10 μm by conversion of bulk material report that the surface still wets i.e., the surface energy remains high. Determination of % weight of oxalic acid, to produce a thin covering is dependent on how oxalic acid will interact with the marble surface. Therefore, consideration has to be given to the molecular dimensions of oxalic acid and the distance between calcium ions in the unit cell. The lattice spacing between the calcium ions is 0.675 nm between rhombohedra ions and ~0.25 nm between the face centred calcium ion and calcium ion of the rhombohedra. The dimension of the oxalate ion, $C_2O_4^{2-}$ is ~0.28 nm. Figure 106 gives the schematic representation of possible interactions of the oxalic acid with the calcite surface. Assuming both groups interact with the surface, ~0.2% w/w of oxalic acid should be approximately equivalent to a monolayer.
DRIFT results reveal common absorption peaks on both the calcium oxalate standard and the resolved coated PIM at 1625 cm\(^{-1}\), 1384 cm\(^{-1}\) and 848 cm\(^{-1}\) and are attributed to the formation of calcium oxalate.

![Figure 107: DRIFT study on the adsorption of oxalic acid on PIM.](image)

No associated carbonyl band of the acid group is observed and both acid groups are assumed to have adsorbed onto the surface.

### 9.2.2.2 XPS Results for PEAA and Oxalic Acid

The broad scan XPS spectra for both coated samples is shown in Figure 108. No impurities are observed and the binding energies and %[atom] are compared to the non-coated PIM, Table 21.
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Figure 108: Broad scan XPS spectra of oxalic acid coated PIM and PEAA coated PIM

<table>
<thead>
<tr>
<th>Element</th>
<th>PIM blank %[atom] Binding energy / eV</th>
<th>Oxalic acid coated %[atom] Binding energy / eV</th>
<th>PEAA coated %[atom] Binding energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>29.9 284.6, 288.6</td>
<td>28.5 284.6, 289.4</td>
<td>68.8 284.6, 290.1</td>
</tr>
<tr>
<td>O</td>
<td>50.2 530.5</td>
<td>50.4 531.3</td>
<td>22.9 531.6</td>
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<tr>
<td>Ca</td>
<td>19.9 346.3</td>
<td>21.1 347.1</td>
<td>8.3 347.5</td>
</tr>
</tbody>
</table>

Table 21: Elemental composition and binding energies for the coated PIM samples as compared to a non-coated sample

Again a shift in binding energies has occurred and is indicative of a coating on the surface. The intensity of the carbon 1s peak for the coating and calcite substrate was determined by curve fitting. Figure 109 and Figure 110 give the results obtained for PEAA and oxalic acid respectively.
The PEAA C1s peak is found to be much more intense than the carbonate C1s indicating a thick layer adsorbed on the surface. The coating intensity is the sum of the two main alkyl groups of the co-polymer fitted individually and the C1s associated with the non-bound acid and surface bound acid, fitted as one peak. The ratio of the polyethylene unit to the polyacrylic acid unit was calculated to be 10:1 respectively. The corresponding XPS fit for the alkyl carbon of polyethylene and the alkyl carbon of the polyacrylic acid gives a ratio of 11:1 and for the carboxylic acid carbon a ratio of 10:1, which agrees well with the calculated ratio.

In comparison the oxalate C1s is much smaller than the C1s of the substrate. The oxalate carbon is shifted to ~ 287.6 eV since it is a diacid with no alkyl carbons and a very thin layer must be present since the intensity of the adventitious C1s is larger.
Using Equation 33, the thickness of each layer was determined and found to be **5.6 nm** for the PEAA and **0.17 nm** for the oxalic acid where the number density is taken to be 0.055 and 0.39 mol cm$^{-3}$ for PEAA and oxalic acid respectively. The PEAA has formed a thick layer on the surface due to the polymer chain length and the high % weight of coating used. The oxalic acid in comparison has formed an extremely thin layer and although most likely forming a monolayer of oxalate ions is unlikely to fully cover the surface of the calcite due its small molecular dimensions.

### 9.2.3 Summary of Coated Samples

Polar functional groups are found to readily adsorb onto the surface of marble powder and therefore present a way in which the surface energy of calcite can be manipulated by having a non-polar section to the coating molecule. With careful control these layers can be in the order of molecular dimensions and
hence they will have no influence on thermal expansion, water vapour transfer and overall aesthetic appearance. PEAA was found to produce the thickest coating, due to the larger polymer chain length and higher % weight used compared to stearate and oxalic acid, and is assumed to fully cover the surface. The thickness of stearate coated PIM varied as a function of % weight of sodium stearate and indicates that the alkyl chains are not orientated vertically to the surface but tend to lie across the surface depending on the concentration of stearate added. 1.1% and 2.2% w/w of sodium stearate gave similar results and is assumed to fully cover the surface where as the 0.55% w/w of sodium stearate may not fully cover the surface and certainly does not react with every calcium ion on the surface. The oxalic acid coating, which was included to represent the naturally formed product scialbatura, does not contain any alkyl component and the interaction with the marble surface will not result in as much of a reduction in surface energy. Additionally layer may not fully cover the surface and as such it is predicted that this will not inhibit acidic gas weathering mechanisms.

Having studied the adsorption of coatings onto the marble surface and characterising the thickness of the layers, the next step was to study their effect on the reaction at the marble surface in the presence of sulphur dioxide.

9.3 Effect of SO$_2$(g) on the Reaction with Coated and Non-coated Marble Powder

9.3.1 DRIFT and XPS Analysis of Reaction Products on non-coated PIM

Diffuse reflectance results were successfully obtained for a range of humidities which, allowing for the dry SO$_2$(g) correction, fall between 5% relative humidity (RH) and >90% RH, which is effectively a saturated atmosphere. Samples were collected for DRIFT analysis every 30 minutes over a three hour period unless otherwise stated and Figure 111, shows the typical spectra obtained after 3hours exposure to 300ppm SO$_2$(g) for the humidity range, where the region of interest is between 900 – 1400 cm$^{-1}$. 
The results have shown that at a relative humidity below 5% RH, SO$_2$(g) does not react with PIM over the duration of the experiment and very little reaction occurs up until 35% RH. This indicates the importance of water as an adsorbed layer on the marble surface, when the gas interacts directly with the surface (‘dry deposition’).

Two main areas of absorption are observed in the DRIFT spectra as a function of exposure time to SO$_2$(g) and % RH. These absorption peaks have been resolved by subtraction of a PIM blank spectrum from each spectrum obtained. The resultant spectra reveal the reaction layer with minimal bulk calcium carbonate contribution to the peak shape and hence allow for better characterisation. The resolved spectra of the two experimental extremes of 35% RH and >90% RH are shown in Figure 112 and Figure 113.
Figure 112: Subtracted DRIFT spectra of reaction products formed at 35% RH over 3 hours.

Figure 113: Subtracted DRIFT spectra of reaction products after exposure to 300 ppm SO2 at >90% RH over 3 hours.
Between 35 - 65% RH the main reaction product has an absorption peak between 900 - 1050 cm\(^{-1}\), and is indicative of a sulphite species. It has been assigned to calcium sulphite. Previous studies of the dry deposition mechanism, under accelerated conditions using characterisation techniques such as X-ray diffraction and anion determination by HPLC, have suggested that calcium sulphite hemihydrate (\(\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}\)) is the species formed in the first stages of reaction\(^{22,201}\).

The recorded spectra were compared to laboratory synthesised calcium sulphite hemihydrate and published data for anhydrous \(\text{CaSO}_3\) and \(\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}\) for complete assignment. The free sulphite ion has \(C_{3v}\) (pyramidal) symmetry, which is lowered on co-ordination in a complex such as the inorganic calcium species. The free ion gives rise to four infrared active fundamental modes, \(v_1\) (symmetric stretch), \(v_2\) (symmetric bend), \(v_3\) (asymmetric stretch) and \(v_4\) (asymmetric bend), where the two asymmetric modes are doubly degenerate\(^{150}\). Table 22 gives the assignment of the observed peaks and reference peak positions.

The experimental absorption frequencies are very complex and suggest that the species formed is not solely the hemihydrate form of calcium sulphite, but possibly a mixture of the anhydrous and hemihydrate sulphite, since characteristic peaks of both compounds are found. No water of crystallisation associated with the hemihydrate, which give sharp peaks at 3387 cm\(^{-1}\) and 1630 cm\(^{-1}\) has been observed. The sulphite species would normally be expected to be that of the hemihydrate since the role of water appears to be vital for the reaction to occur. However at low relative humidities it may be possible that insufficient water is adsorbed on the surface such that the formation of the hydrated sulphite occurs in patches effectively forming an amorphous phase that results in the broadening of the water peaks. Possible mechanisms are discussed in section 9.3.2.1.
Typical Experimental \[ \text{Lab synthesised CaSO}_3 \text{ cm}^{-1} \] Anhydrous CaSO\(_3\) \[ \text{ cm}^{-1} \] CaSO\(_3\) \[ \text{cm}^{-1} \] \[ \text{Peak assignment} \] 

<p>| | | | |</p>
<table>
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<td></td>
<td>3387.4</td>
<td>3389</td>
<td>O-H stretch</td>
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<td></td>
<td>1630</td>
<td>1630</td>
<td>O-H bend</td>
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<td>1012</td>
<td>( v_1 ) symmetric stretch S-O</td>
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<td>982</td>
<td>( v_3 ) asymmetric stretch S-O</td>
</tr>
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<td>( v_3 ) asymmetric stretch S-O</td>
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<td>combination of ( v_1 ) and ( v_3 ) O-S-O stretch</td>
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<td>( v_3 ) asymmetric stretch</td>
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<td>( v_3 ) asymmetric stretch</td>
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<td>Bend</td>
</tr>
<tr>
<td>649</td>
<td>649</td>
<td></td>
<td>Bend</td>
</tr>
</tbody>
</table>

Table 22: Peak assignment for sulphite species by comparison to laboratory synthesised and published results

As the relative humidity is increased above 65%, reaction with \( \text{SO}_2(g) \) produces two separate species. First is the sulphite species where the absorbance peak is between 900 – 1050 cm\(^{-1}\). The second species has an absorbance peak between 1080 – 1250 cm\(^{-1}\) and is characteristic of calcium sulphate. The corresponding sharp peaks between 3200-3700 cm\(^{-1}\) and two peaks at 1622 cm\(^{-1}\) and 1682 cm\(^{-1}\), are indicative of water of crystallisation and shows that the calcium sulphate is the dihydrate, gypsum, Figure 114. Analysis of weathered layers from the Ince collection, also found the alteration product to be that of calcium sulphate dihydrate, and peak assignment can be found in Chapter 7. The reaction peaks observed at 1171, 1140, 1121.3 and 985 cm\(^{-1}\) under accelerated conditions are comparable to those obtained for the reference spectra and published data for gypsum.
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Figure 114. Resultant DRIFT spectra after PIM blank subtraction. Calcium sulphate dihydrate and calcium sulphite formation after 3 hours exposure to 300 ppm SO₂ at >90% RH

XPS spectra were also recorded for the marble powder exposed to SO₂(g) and sulphur is detected, Figure 115.

Figure 115: XPS broad scan spectrum of PIM after 180 minutes exposure to SO₂(g) at 85% RH
High resolution spectra of the sulphur 2p gives a broad line shape that is attributed to a doublet that comprises the $2p_{3/2}$ and $2p_{1/2}$ photoelectrons, which means the peaks are only partially resolved. The separation of the doublet is 1.2 eV, Figure 116. However as can be seen from the peak fit which takes account of the contribution of the $2p_{3/2}$ and $2p_{1/2}$ peak, two species are present, each as a doublet, resulting in a broad peak with a low signal to noise ratio. The low signal to noise ratio on the high resolution sulphur 2p peak spectra has made quantitative characterisation at the lower humidities difficult. However the 85% RH, as discussed in the next section, has been characterised and the measured binding energy of the two species, charged referenced to adventitious carbon, are 166.6 eV and 168.8 eV. These values agree reasonably well, considering the very low signal to noise, with the measured standards of calcium sulphate hemihydrate and calcium sulphate dihydrate, with binding energies of 167.1 and 168.8 eV respectively.

Figure 116: High resolution S2p XPS spectrum of PIM reacted with SO$_2$ at 85% RH.
9.3.2 DRIFT Analysis of Reaction Products as a Function of Time and Relative Humidity.

To assess the effectiveness of monolayer coatings it is important that the species formed on reaction with SO$_2$(g) can be followed quantitatively and so DRIFT spectra have been quantitatively analysed for each humidity experiment at all time intervals. The ratio of peak area of interest to the carbonate peak at 713 cm$^{-1}$ compensates for errors due small inconsistencies in sample preparation. The resultant peak ratio can be used as a measure of the amount of sulphate and sulphite species present, when their concentrations are low, and have been plotted against time for each humidity experiment in Figure 117 to Figure 124.

![Graph showing DRIFT peak integration of sulphite species formed over 3 hours at 35% RH.](image)

At 35% RH only calcium sulphite is detected. The lack of calcium sulphate suggests that the sulphite formed does not appear to oxidise readily to the sulphate during three hours, which may indicate either insufficient adsorbed
water for continued reaction, or that the sulphate forms via a different mechanism.

For 55% and 65% RH, Figure 118 and Figure 119 respectively, calcium sulphite remains the predominant product formed over all time periods and the overall concentration is found to increase with humidity. Only a small amount of calcium sulphate is observed after an initial latent period and the product does not appear to significantly increase in concentration over the observed reaction time. No associated water of crystallisation could be detected by DRIFT spectroscopy and it would appear that the measured concentration of calcium sulphate is near the limit of detection.

Figure 118: DRIFT peak integration of sulphate and sulphite species formed at 55% RH
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Figure 119: DRIFT peak integration of sulphate and sulphite species at formed 65% RH

The data points, although increasing, do not increase linearly and appear to plateau before increasing in rate again. The reason for this is not entirely clear from the results available, and there may be many possible explanations. One possibility could be due to how the reaction products form on the calcite surface. During the initial stages of reaction the formation of the products may occur in patches on the surface creating islands of alteration products. As the alteration layer completely covers the surface the reaction may be expected to plateau and any further reaction will occur by gas diffusion through the reacted layers or calcium ion dissolution from the bulk to the surface. Or detachment of small particulates of calcium sulphite from the surface may lead to a ‘fresh’ surface for reaction. Whilst this is an intriguing result the main point is that the overall sulphite concentration increases with increasing humidity.

At 75% RH, Figure 120, the reaction profile changes. Calcium sulphite is still the predominant species being formed, and at a greater rate than at previous
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humidities. In addition to calcium sulphite formation calcium sulphate dihydrate is also observed. Noticeably the concentration of calcium sulphate dihydrate increases with increasing time, without a change in the reaction profile of sulphite and is indicative of the formation of both species independently of one another, rather than the oxidation of the sulphite to the sulphate.

At 85% RH Figure 121, sulphite is no longer the predominant species over all time intervals. The initial rates of formation of both species are found to be similar up until 120 minutes exposure, again at higher concentrations than previous humidities. After 120 minutes, the formation of the sulphate species is found to increase in rate whereas the sulphite concentration continues to increase, but noticeably at a similar rate of formation compared to 75% RH. This reinforces the theory that the formation of the two species form independently of one another and may actually undergo a competition process for formation, dependent on the relative humidity.

Figure 120: DRIFT peak integration of sulphate and sulphite species formed at 75% RH
XPS spectra were also recorded for samples removed every 30 minutes from PIM exposed to SO$_2$(g) at 85% RH. From the plot of %[S] against time, the sulphur concentration due to the alteration products increases to a maximum of 46 atom % of the total surface composition, Figure 122.
By amending Equation 33, for the attenuation length of photoelectrons in the sulphate and sulphite layer, the number atom density and the relative sensitivity factor, it has been possible to estimate a thickness for the alteration layer, Equation 34. This assumes that the alteration layer develops evenly across the surface and not in patches on the surface.

\[
\frac{I_s}{I_c} = \frac{RSF_s}{RSF_c} \frac{n_s \lambda_s}{n_c \lambda_c} \frac{\frac{\pi}{2} \left[ \cos \theta \sin \theta \left( 1 - \exp \left( -\frac{d}{\lambda_s \sin \theta} \right) \right) \right]}{\frac{\pi}{2} \left[ \cos \theta \sin \theta \left( \exp \left( -\frac{d}{\lambda_c \sin \theta} \right) \right) \right]} d\theta
\]

Equation 34: Spherical model for sulphur species on a marble surface
Where $RSF_S = 0.44$ and is the relative sensitivity factor for $S\ 2p$, $RSF_C = 0.23$ and is the relative sensitivity factor for $C\ 1s$. $n_s$ is the number atom density for sulphate and sulphite and is taken to be $0.0135\ mol\ cm^{-3}$ and $n_c$ is the number atom density for calcium carbonate and is taken to be $0.027\ mol\ cm^{-3}$. The attenuation length is calculated according to Seah et al.\ 130 and $\lambda_s$, the attenuation length in the sulphate/sulphite layer is $2.64\ nm$. $\lambda_s'$, the attenuation length of carbon through the sulphate layer is $2.54\ nm$. $\lambda_c$, the attenuation length in calcium carbonate is $2.67\ nm$.

![Graph]

**Figure 123**: Spherical model results for determination of alteration layer thickness on PIM

The ratio of peak intensities of the peak fitted $S\ 2p\ (I_s)$, incorporating the contribution of both $SO_4^{2-}$ and $SO_3^{2-}$, and the peak fitted $C\ 1s\ (I_c)$ can be compared to the values obtained from the spherical model results shown in Figure 123. Curve fitting of the peaks from the sample removed after 180 minutes gave a measured peak ratio of $0.54$, which from Figure 123, corresponds to a thickness of $\sim 0.7\ nm$. If 100% reaction between $SO_2(g)$ and PIM occurred the theoretical thickness of the alteration product would be $\sim 32\ nm$, assuming an even coverage.  
Comparison to the experimentally determined
thickness therefore indicates that approximately 2% of the SO$_2$(g) actually reacts with the marble surface under these accelerated conditions. This compares favourably to the reported data of Hutchinson et al. who observed an SO$_2$ absorption of 1-2% of total SO$_2$ available at 25 ppm and 95% RH.

When the relative humidity becomes greater than 90% a completely different reaction mechanism appears to occur with the formation of the sulphate species predominating the reaction. The measured peak ratio is found to be significantly greater than any other relative humidity. In comparison the level of sulphite formed is comparable to that formed at 55% RH. Near to the saturated vapour pressure the adsorption of water onto the surface is greatest and it can be assumed that multilayers of water are present on the surface such that the SO$_2$(g) dissolves rapidly to form sulphuric acid which reacts directly to give calcium sulphate dihydrate. Adsorbed water cannot be detected due to the presence of the water of crystallisation peaks associated with the sulphate species, in the same frequency range.

![Figure 124. DRIFT peak integration of sulphite and sulphate species at >90% RH where insert magnifies the sulphite formation](image)
9.3.2.1 Summary of reaction products formed as a function of relative humidity.

By varying the relative humidity it has been possible to study the reaction in relation to the amount of water adsorbed on the surface. To summarise the effect of relative humidity on the reaction of $\text{SO}_2(\text{g})$ at the calcite surface the peak ratio is plotted against % RH for the reaction after 60, 120 and 180 minutes, Figure 125, Figure 126 and Figure 127 respectively.

![Figure 125: Effect of relative humidity on the formation of reaction products after 60 minutes](image-url)
Figure 126: Effect of relative humidity on the formation of reaction products after 120 minutes

Figure 127: Effect of humidity on the formation of reaction products after 180 minutes
Therefore with increasing relative humidity a number of observations are made:

1. The concentration of each species increases with increasing RH up until 90% RH. At >90% RH a separate mechanism occurs that favours the formation of gypsum and whilst calcium sulphite still forms this concentration is comparable to 55% RH.

2. The sulphite formation dominates the reaction up to humidities < 80% RH with very little sulphate present.

3. There appears to be no correlation between the formation of both species and it is suggested that both are forming independently.

4. At humidities > 90% the reaction is dominated by the rapid formation of calcium sulphate dihydrate where the concentration of this species is much greater than the total concentration observed at all other relative humidities.

The variation in reaction with relative humidity implies that it is the amount of adsorbed water on the marble surface that determines the extent of reaction and the reaction mechanism for SO$_2$(g) when it is adsorbed by ‘dry deposition’. The role of water is generally accepted as important in the formation of calcium sulphate although its affect on these mechanisms is still ambiguous\textsuperscript{22,201,35,50,52,8,55,202}. Repeating the general equations usually quoted which take no account of stoichiometry, the formation of products is given by.

\[
\begin{align*}
1. & \quad \text{CaCO}_3(\text{s}) + \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \xrightarrow{\text{aq}} \text{CaCO}_3(\text{s}) + 2\text{H}^+\text{SO}_4^{2-(aq)} + 2\text{H}_2\text{O}(\text{l}) \\
& \quad \downarrow \\
& \quad \text{CaSO}_4\text{.2H}_2\text{O}(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O} \\
2. & \quad \text{CaCO}_3(\text{s}) + \text{SO}_2(\text{g}) \xrightarrow{\text{H}_2\text{O}} \text{CaSO}_3\text{.H}_2\text{O}(\text{s}) + \text{CO}_2(\text{g}) \xrightarrow{\text{O}_2(\text{g})} \text{CaSO}_4\text{.2H}_2\text{O}
\end{align*}
\]
As shown in the above equations the formation of sulphite is believed to be present only as an intermediate in the formation of the eventual product calcium sulphate dihydrate. Analysis of the Ince Blundell collection did not reveal the presence of any calcium sulphite on the surface of the weathered marble. To test the above equations hypothesis that the sulphite species converts to the sulphate in the presence of oxygen a sample was reacted for the normal 3 hour period at 85% RH. After this period the SO$_2$(g) flow was stopped and the sample exposed to the air flow at 85% RH for a further 3 hours and samples removed every 30 minutes. It was found that there was no significant change in the peak ratio for either compound, Figure 128. Even after exposure to air in the laboratory for three months there was only a conversion of 2% to the sulphate. This result compares to the findings of Elvfing et al., who reported that molecular oxygen was too weak an oxidant to convert the sulphite to the sulphate$^{51,203,204}$. They reported that under more oxidising reagents such as ozone, the sulphite is rapidly converted to the sulphate either in dry or humid environments and others report that in the presence of metal chlorides and other catalysts deposited in the gypsum crust the conversion is significantly accelerated$^{205}$. XPS analysis has detected the presence of chlorides, on the Ince Blundell collection, due to the marine environment and ozone is a known atmospheric pollutant and any sulphite formed is most likely converted to the sulphate under such conditions. Therefore it is possible for calcium sulphate dihydrate to form independently of calcium sulphite when the SO$_2$(g) interacts directly with the marble surface (dry deposition) rather than by acid rain (wet deposition).
The mechanism of formation of the two species and why the sulphite group forms in preference to the sulphate group at lower humidities is still equivocal, other than water has a vital role. Therefore the influence of water has been considered in more detail.

The exact type of water i.e. physisorbed or chemisorbed, was still unclear from these results and further attempts were made to characterise the water associated with the reaction. DRIFT spectra taken as a function of relative humidity only, on ambient temperature vacuum dried PIM, reveal very small peaks in the region between 3200 – 3700 cm\(^{-1}\). At a humidity above 90% RH a broad peak across the whole region is observed whereas below this level there appears to be two poorly resolved peaks at 3220 cm\(^{-1}\) and 3425 cm\(^{-1}\) with a small shoulder at 3620 cm\(^{-1}\), Figure 129.
Figure 129: DRIFT spectra of water absorption in the region 3100 – 3700 cm\(^{-1}\) for varying humidity

These peak positions correspond to those observed by Neagle and Rochester where the maximum at 3450 cm\(^{-1}\) is ascribed to the OH-stretching vibrations of bulk or surface water where even after evacuation at ambient temperatures hydroxyl groups were still present\(^{149}\). These were found to be predominantly bulk water in the crystal lattice. Generally the bands observed in Figure 129, can be assigned to both chemisorbed hydroxyl groups which show hydrogen bonding and associatively adsorbed water molecules at the calcite surface.

Morimoto \textit{et al.}\(^{206}\) calculated, from water adsorption isotherms, between 5-9 OH groups / nm\(^2\) of the calcite surface where for natural calcite the surface density of each of the Ca\(^{2+}\) and CO\(_2\)^{2-} ions is \neg15 ions / nm\(^2\). Water molecules, in the first monolayer, associated with the surface hydroxyl groups were calculated to either physisorb onto one or two hydroxyl groups.

An attempt to quantify the level of physisorbed water as a function of humidity was made as part of this study on PIM using a microbalance. However results proved inconclusive and was attributed to the low surface area of the calcite
and the difficulty in maintaining a stable mass reading for the low mass of sample used. However Ashan's study of the surface properties of a high surface area, precipitated calcite by the adsorption of water vapour reports the amount of water adsorbed on a surface area of 28 m² g⁻¹. These results have been used to estimate the water adsorption layer thickness on PIM as a function of humidity and the results are plotted in Figure 130.

Figure 130: Estimation of water layer thickness adsorbed onto the calcite surface as a function of % RH

The water molecule radius can be regarded as 0.14 nm, and hence at 35% RH the level of physisorbed water is approximately one molecular layer assuming water adsorption estimation is valid. As the relative humidity increases, two monomolecular layers do not form until approximately 75% RH, this presumes that water is physisorbed in thin uniform layers and it is possible that localised clusters of water molecules form on the surface. Above 75% RH as the humidity approaches a saturated atmosphere water adsorption occurs.
more readily until at greater than 90% RH multilayer adsorption is observed. This level of water adsorption allows some mechanistic conclusions to be drawn for the observed species formed at varying relative humidities.

Calcium sulphate was not significantly formed at the lower humidities and from Figure 130, this can most probably be attributed to the level of physisorbed water, which is effectively the rate determining step. Figure 131, gives a possible mechanism for the formation of the sulphate anion, which involves aqueous reactions. At low %RH, the extent of water adsorption is only in the order of one or two monomolecular layers, and must therefore be insufficient for the formation of hydrated $SO_3^{2-}$ and $SO_4^{2-}$ anions. In solution both have been reported to have has many as 8 water molecules in the hydration sphere$^{210}$. Additionally oxygen has to adsorb into an aqueous layer to oxidise the sulphite anion to the sulphate anion and a thin layer most likely affects this as well. Not until there are more than two monolayers of water is there sufficient solution to allow hydration of the ions and resultant diffusion to the surface for reaction. This fits the observed DRIFT results where, sulphate is detected in appreciable amounts at a relative humidity of 75% or greater. At a humidity above 90% where multilayer adsorption occurs the level of water is such that it is no longer the rate determining step.

\[
\begin{align*}
SO_2(g) + H_2O & \rightleftharpoons SO_2H_2O \\
SO_2H_2O & \rightleftharpoons H^+(aq) + HSO_3^-(aq) \\
HSO_3^-(aq) & \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \\
SO_3^{2-}(aq) + \frac{1}{2}O_2(g) & \rightleftharpoons SO_4^{2-}(aq)
\end{align*}
\]

Figure 131: Proposed formation of sulphate anion in a thin water layer on the calcite surface
For the formation of calcium sulphite hemihydrate the level of water required for reaction is significantly less. Previous research for the oxidation mechanisms of SO$_2$(g) in the atmosphere, on aerosol particles and calcium oxide and calcium carbonate used in gas flue scrubbers, have postulated mechanisms for the formation of calcium sulphite$^{209,211,212}$. It is suggested that SO$_2$(g) adsorbs onto the surface to form a water complex with one molecule of water, and that the formation of sulphite proceeds directly at the surface and the suggested reaction is given in Figure 132. A similar mechanism would be consistent with the results presented here, where sulphite is observed to form at low relative humidities where water adsorption is also low.

$$\begin{align*}
H_2O(g) & \rightleftharpoons H_2O(ads) \\
SO_2(g) & \rightleftharpoons SO_2(ads) \\
SO_2 H_2O_{(ads)} + Ca(OH)_{2(surface)} & \rightarrow CaSO_3 + 2H_2O
\end{align*}$$

Figure 132: Formation of calcium sulphite by gas adsorption at the calcite surface

The mechanism by which non-coated calcite reacts with sulphur dioxide is complex with the level of adsorbed water playing a vital role in which species is formed and to what extent they form. DRIFT spectroscopy can follow the reaction quantitatively and therefore allows the coated PIM samples to be assessed under the same conditions.

9.3.3 DRIFT and XPS Analysis of Coated Marble Powder Exposed to SO$_2$(g) at 85% RH.

The coated samples were reacted at 85% RH since the non-coated PIM reacted to produce both species at comparable concentrations.

For the stearate coated PIM all three samples, coated with varying % w/w of sodium stearate, totally inhibited the formation of calcium sulphate over the
reaction period, but only slowed the rate of formation of calcium sulphite. Figure 133.

![Graph showing effect of Stearate coating on the reaction of SO₂(g) on PIM at 85% RH](image)

In terms of formation of calcium sulphite, the integrated peak ratio after 180 minutes reaction was found to be 0.63, 0.47 and 0.26 for 0.55%, 1.1% and 2.2% w/w coated PIM respectively. These compare to the non-coated integrated peak ratio of 0.9 after the same exposure time. Therefore coating at 0.55% w/w reduces the formation of sulphite by a factor of 1.4, a coating level of 1.1% reduces the sulphite formation by approximately half whilst 2.2% w/w reduces the sulphite formation 3.5 times. Two points can be noted from this experiment:

1. No calcium sulphate was observed on any of the samples  It is suggested that the conformation of the adsorbed stearate molecules must nearly or
completely cover the surface, hence reducing the surface energy such that water does not tend to adsorb.

2. The formation of calcium sulphite is not completely hindered and hence there must be some free calcium ion reactive surface sites where stearate molecules have not adsorbed or cannot adsorb due to the area occupied by other adsorbed stearate molecule head groups (20 x 10^{-20} m^2). Where the coating level is smallest, 0.55% w/w, the number of free reactive sites is greatest and the mechanism outlined in Figure 132 can occur. As the coating level increases these reactive sites are reduced and hence the extent of reaction reduces. It would be interesting to continue to increase the %w/w of sodium stearate to see if it is possible to occupy all surface calcium ions such that calcium sulphite formation can also be completely hindered.

The PEAA coated sample was also found to inhibit the formation of calcium sulphate dihydrate and only slow the rate of formation of calcium sulphite, Figure 134. The overall reaction profile lies somewhere in-between that observed for the 1.1% and 2.2% w/w sodium stearate covered PIM. Even though PEAA gives a much thicker layer the overall benefit is comparable to the stearate layers that are approximately 4 - 5 times thinner.
RESULTS AND DISCUSSION

Chapter 9 WEATHERING PROTECTION USING MONOLAYER COATINGS

Figure 134: Effect of PEAA coating on the reaction of SO$_2$(g) with PIM at 85% RH

For the oxalic acid coated PIM the reaction at 85% RH is not inhibited and both calcium sulphate dihydrate and calcium sulphite are formed over the reaction period, Figure 135. The main reaction product after 180 minutes exposure to SO$_2$(g) is found to be calcium sulphite whereas for non-coated PIM calcium sulphate dihydrate is the predominant species formed. This may indicate that the calcium oxalate has some influence on the reaction mechanism. The fact that neither mechanism is totally inhibited, suggests that water adsorption and some calcite dissolution occurs. Even though many of the surface calcium ions are occupied by the coating, carbonate anions are not covered and can be dissolved allowing further dissolution of lattice ions and possibly aqueous phase formation of calcium sulphite and calcium sulphate.
To compliment the analysis by DRIFT, XPS was also used to study reaction products after the maximum exposure time and again low signal to noise made quantification of individual species difficult. The total $\%[S]$ detected is compared to the non-coated powdered marble and results are shown in Figure 136. Results show that the reaction does decrease with the addition of the stearate and PEAA overlayers but that coating with a monomolecular layer of oxalic acid is comparable to the non-coated PIM.
9.4 Summary

With careful control, coatings can be applied to a marble surface to alter the surface energy. Three different coatings have been studied, that derive from either naturally formed degradation products or ancient bulk preservation treatments. Combining the use of DRIFT spectroscopy and XPS it has been possible to characterise their adsorption and quantify the thickness of these adsorbed layers. Table 23, summarises the determined thickness and shows that layers in the order of molecular dimensions can be achieved. Hence effects on weathering due to differences in thermal expansion and pore filling are minimised, and no surface crust or aesthetic differences are observed.
Chapter 9 WEATHERING PROTECTION USING MONOLAYER COATINGS

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness of layer / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55% w/w sodium stearate</td>
<td>~0.55</td>
</tr>
<tr>
<td>1.1% w/w sodium stearate</td>
<td>~1.15</td>
</tr>
<tr>
<td>2.2% w/w sodium stearate</td>
<td>1.4</td>
</tr>
<tr>
<td>9% w/w PEAA</td>
<td>5.6</td>
</tr>
<tr>
<td>0.25% w/w Oxalic acid</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 23: Summary of differing coating thickness applied to PIM

How these coatings affect the interaction of acidic gases with the marble surface under ‘dry deposition’ conditions has also been quantitatively studied by DRIFT spectroscopy. Non-coated marble is observed to undergo a complex reaction mechanism, where the level of adsorbed water is the fundamental property that controls the extent and type of reaction mechanism (Hence the study of stearate and PEAA coatings, which reduce water adsorption). Calcium sulphite and calcium sulphate can form independently under dry deposition conditions. The suggested mechanisms show that sulphite formation only requires one water molecule, whilst for sulphate formation complete layers of water greater than 2 mono layers thick are required. Hence sulphite formation predominates at low humidities whilst sulphate formation predominates at high humidities where multilayer adsorption occurs.

The coated samples were reacted with $SO_2(g)$ at 85% RH, and quantitatively analysed by DRIFT spectroscopy, where the results were compared to the non-coated sample at 85% RH. The stearate coated samples and PEAA stopped the formation of calcium sulphate and slowed the formation of calcium sulphite. The observed sulphite reaction is attributed to free surface calcium ions not occupied by the adsorbed coating and it is suggested that the % w/w of sodium stearate be increased further to see if all reactive sites can be occupied and the reaction completely inhibited. The oxalic acid coating did not produce any
significant effect on the inhibition of reaction mechanisms and it is suggested that where these layers exist naturally it is the thickness (often greater than 10 μm) that slows the reaction, by limiting the diffusion of reactive gases to the surface.

In terms of application onto an actual sculpture, consideration should be given to the method of coating. For example, the above model study uses a water-based system, which will only allow for one application before the surface becomes less likely to wet. It is suggested that stearic acid can be applied in a toluene solvent system, since this has been found to be a possible way to coat calcite and will allow for further applications\(^{196}\). Therefore by controlling the concentration applied by either estimating the porosity or directly measuring the porosity no pore filling can occur. This will allow the marble to “breathe” whilst inhibiting water adsorption onto the surface, which has been observed to be the main precursor in the mechanism of chemical alteration.
Chapter 10 CONCLUSIONS

This thesis has been based on two fundamental areas of research:

1. The development of a consolidation procedure
2. The development of protective coatings

These two areas have been addressed in response to the condition of many sculptures from Ince Blundell collection. Typically, the surface has become highly friable with almost complete loss of crystal cohesion and significant loss of sculptural detailing. Samples from the collection have been characterised using surface techniques, which have provided important data for research in the above two areas.

10.1 Development of a Consolidation Procedure.

The new approach to marble consolidation uses charge stabilised colloidal dispersions of synthetically precipitated calcite, followed by application of limewater and carbon dioxide. The first step is to significantly reduce the overall porosity of the weathered marble by the deposition of individual particulates deep into the friable areas. The second step is used to nucleate and grow calcite crystals onto the particles and bridge across to the original substrate. Theoretical considerations and experimental measurements of colloidal stability and particle size in relation to pore size have identified the optimum conditions for both steps. The van der Waals and electrostatic interaction energies have been estimated for the colloidal dispersion interaction and particle/marble surface interaction.
Characterisation of small treated fragments indicate the penetration of particles into the bulk material rather than accumulation on the surface.

The technique has been proven to work on a small scale in the laboratory, consolidating the extremely friable area on a 2nd Century Roman bust from the Ince Blundell collection. Two years after the initial consolidation, the treated area is still in good condition. The conservation section of NMGM has now scheduled external field trials at the Ince site, on the carvings located either side of the pantheon as pictured in Figure 28.

The principle advantage of this method is that it is sympathetic to the work of art, introducing minimal foreign material. The amount of consolidant applied can be easily controlled such that surface crust formation is avoided. By only introducing calcite into the porous network, issues such as thermal expansion coefficients, colour alterations and density differences do not occur. It is realised that if a consolidated sculpture was to be placed back into its original environment, weathering mechanisms will still continue, and so the second part of the research focused on protective coatings.

10.2 Protective Coatings

Since water appears to be the main precursor for many weathering mechanisms the formation of a hydrophobic layer to inhibit the action of water was an obvious route to investigate. Many ancient treatments and more recent methods involved the application of thick hydrophobic coatings that often resulted in as many detrimental effects as advantageous ones. The focus of this research assessed the effects of monolayer thick coatings on the inhibition of calcium sulphate formation.

This section of research was subdivided into two areas:

1. The characterisation of monolayer coatings on powdered marble, to study coating adsorption and layer thickness. DRIFT spectroscopy and XPS were
both used successfully in this area. The coatings tested all were observed to form a calcium salt surface species, and the thickness of these layers ranged from 0.17–5.6 nm.

2. The study of the weathering mechanism on coated and non-coated powdered marble under extreme conditions of $\text{SO}_2(\text{g})$ at varying humidity. Growth of calcium sulphite and calcium sulphate on the non-coated sample was observed, varying as a function of relative humidity. Semi-quantitative analysis via DRIFT spectroscopy proved a successful technique for the study of reaction products. Under the conditions used in this study no evidence has been found for the formation of calcium sulphate through a sulphite intermediate. Consideration of the water layer thickness on the marble surface in relation to the dissolution and hydration of surface and pollutant species has be used to postulate the mechanisms involved.

The stearate and PEAA coatings are both effective in stopping all calcium sulphate formation, under these experimental conditions, and reduce calcium sulphite formation. It is suggested that the hydrophobic surface, limits water adsorption and is the probable reason for their effectiveness.

The overall aim of the research was to be as sympathetic to the original marble by the application of minimal foreign material. Application of monolayer thick coatings introduces the minimum possible material that will significantly reduce weathering. The stearate coating can be applied using non-aqueous solvents making its application easier. The resulting hydrophobic surface will not block the pores, allowing water vapour to pass freely through the stone, additionally there is no surface crust formation or colour alteration.
10.3 Further Work

Both areas have produced promising results and further research could be carried out.

In terms of the consolidation procedure further investigation by mercury porosimetry to determine porosity reduction is important, provided a large enough sample for reproducible experimentation can be obtained. Additionally, the application order of the PCC dispersion and limewater solution could also be studied in relation to increase in mechanical strength. For example, alternate application of PCC followed by limewater may produce a more rigid structure.

An interesting observation from this research was the colloidal stability observed for PCC dispersed in methanol and methanol water mixes. The dispersion remained stable for many weeks, maintaining the particles in their individual state. Application to a porous surface could result in much deeper penetration. Study of the dispersion and intermolecular forces would be very interesting.

For the protective coatings, longer trials are required to fully test their effectiveness. Additionally, the effectiveness on the inhibition of other chemical weathering mechanisms such as NO$_2(g)$ and HCl would be recommended. Since the coatings produce a hydrophobic surface, the action against biological weathering could also be investigated.
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APPENDIX 1: XRD Analysis

Powder x-ray diffraction was carried out on the powdered Italian marble and precipitated calcium carbonate. The run was scanned from 20-40° (2θ) at 2° per minute. Results were compared to standard powder x-ray diffraction files.

**Powdered Italian Marble**

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>2-theta Angle</th>
<th>Raw intensity</th>
<th>d-space</th>
<th>Relative intensity</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>21.55</td>
<td>48</td>
<td>4.12</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>23.35</td>
<td>132</td>
<td>3.806</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>26.9</td>
<td>45</td>
<td>3.312</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>29.7</td>
<td>1098</td>
<td>3.006</td>
<td>100</td>
</tr>
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<td>5</td>
<td>31.8</td>
<td>61</td>
<td>2.812</td>
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</tr>
<tr>
<td>6</td>
<td>36.3</td>
<td>141</td>
<td>2.473</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>39.75</td>
<td>161</td>
<td>2.266</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>43.5</td>
<td>140</td>
<td>2.079</td>
<td>13</td>
</tr>
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**Precipitated CaCO₃**

The run was repeated using the same parameters as before.

<table>
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<th>2-Theta Angle</th>
<th>Raw Intensity</th>
<th>d-space</th>
<th>Relative Intensity</th>
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<td>1</td>
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<td>3.815</td>
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<td>2</td>
<td>26.75</td>
<td>57</td>
<td>3.33</td>
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<td>29.7</td>
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<td>100</td>
</tr>
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<td>4</td>
<td>30.25</td>
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<td>2.952</td>
<td>5</td>
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<td>31.8</td>
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<td>2.812</td>
<td>7</td>
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<td>6</td>
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<td>2.53</td>
<td>5</td>
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<td>37</td>
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<td>196</td>
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Reference powder x-ray diffraction files

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<th>S.G. D₃̃₃d - R3c</th>
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<td>b₀</td>
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<td>(natural)</td>
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<tr>
<td></td>
<td></td>
<td>β 16.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>γ 6.13</td>
</tr>
<tr>
<td></td>
<td>Rad: CuKα₁</td>
<td>λ: 1.5405</td>
</tr>
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<td></td>
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</tr>
<tr>
<td>dÅ</td>
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</tr>
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<td>100</td>
</tr>
<tr>
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<td>104</td>
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<table>
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<th>S.G. R₃c(167)</th>
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<td>b₀ 9.966</td>
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<tr>
<td>(synthetic)</td>
<td>c₀ 17.002</td>
<td>α 17.392</td>
</tr>
<tr>
<td></td>
<td>β 16.54</td>
<td>γ 6.13</td>
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<td></td>
<td>Rad: CuKα₁</td>
<td>λ: 1.5405</td>
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<td>100</td>
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<td>111</td>
<td>2</td>
<td>4</td>
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<tr>
<td>2θ</td>
<td>4.212</td>
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</tr>
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<table>
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<tr>
<th>5-454: CaCO₃</th>
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<th>S.G. D₄₂₁ - PMNC</th>
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<td>b₀ 7.966</td>
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<td>c₀ 5.741</td>
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<tr>
<td></td>
<td>β 16.54</td>
<td>γ 0.721</td>
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<td>Rad: CuKα₁</td>
<td>λ: 1.5405</td>
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<td>dÅ</td>
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<td>I/I₀</td>
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<table>
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<th>S.G. P6₃/mmc</th>
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<td>b₀ 8.49</td>
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<td>(synthetic)</td>
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<td>α 17.392</td>
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<td></td>
<td>β 16.54</td>
<td>γ 6.13</td>
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<td>Rad: CuKα₁</td>
<td>λ: 1.5405</td>
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<td>004</td>
</tr>
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<td>112</td>
</tr>
</tbody>
</table>
Appendix 2 : Poisson-Boltzmann Equation.

The first fundamental equation for description of the electrical double layer, where the local electrostatic potential $\psi$ at any point $x$ from the surface in the diffuse layer is given by:

$$\frac{d^2 \psi}{dx^2} = \frac{2ze_n_0}{\varepsilon} \sinh \left( \frac{ze_\psi_0}{kT} \right)$$  \hspace{1cm} \text{Equation 1: P-B equation}

Where $z$ is the ion charge, $e$ is the charge on an electron, $n_0$ is the bulk concentration of each ionic species and is known as the Poisson–Boltzmann distribution (P-B eqn.), which is a combination of individual equations 9 and 10. The Poisson equation gives the potential at point $x$ related to the net volume charge density, $\rho$, in the diffuse layer.

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho}{\varepsilon}$$  \hspace{1cm} \text{Equation 2: Poisson equation}

The net volume charge density is however an unknown, but can be obtained by assuming that the distribution of ions obeys Boltzmann’s law, where the number density of cations and anions at $x$ can each be determined from the Boltzmann equation.

$$n_i x = n_i 0 \exp \left[ -\frac{z_i e \psi}{kT} \right]$$  \hspace{1cm} \text{Equation 3: Boltzmann equation}

The exponential term relates the electric potential energy term, $ze_\psi$, (which represents the work done in bringing an ion $i$ up from the bulk solution to $x$ in the diffuse layer), to its entropic thermal energy kT. When the ion has a sign opposite to the sign of the surface potential the local concentration of counter-
ions is always higher than the corresponding co-ion. This is related to charge density in the diffuse layer since.

\[ \rho = ze(n_+ - n_-) = -2ze n_0 \sinh \left( \frac{ze \psi}{kT} \right) \]  
Equation 4

The P-B expression is a second order differential equation, which with the following boundary conditions can be solved \( \psi = \psi_0 \) at \( x = 0 \) and secondly \( \psi = d\psi/dx = 0 \) at \( x = \infty \). This gives

\[ \psi = \frac{2kT}{ze} \ln \left( \frac{1 + \gamma \exp[-\kappa \xi]}{1 - \gamma \exp[-\kappa \xi]} \right) \]  
Equation 5

Where

\[ \gamma = \frac{\exp[ze \psi_0 / 2kT] - 1}{\exp[ze \psi_0 / 2kT] + 1} \]  
Equation 6