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LASER CLEANING OF STONE SCULPTURE

by

Martin Ian Cooper

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy at the Loughborough University of Technology.

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Abstract

This thesis is concerned with different aspects of laser cleaning of stone sculpture including the interaction of laser radiation with stone, evaluation and monitoring of the cleaning process and the development of a practical cleaning tool.

Results show that a Q-switched Nd:YAG laser is the most suitable type of laser for the removal of black encrustations from marble and limestone surfaces. Measurements of the absorptivity of polluted and clean stone surfaces at 1.06 μm show that a typical black crust, resulting from atmospheric pollution, absorbs 2.5-3.5 times as much of the incident radiation as typical clean limestone and marble surfaces. This is shown to lead to the controlled removal of black crust material, by several thermal and mechanical mechanisms, without damaging the underlying stone. Measurements of ablation thresholds, by deflection of a probe beam, reveal that material is removed from a black crust at a fluence approximately half that required to remove material from a clean limestone or marble surface.

Monitoring of the acoustic pulse generated during the laser beam/stone interaction is used to characterise the cleaning process. Results also show that cleaning is more efficient when a thin layer of water is applied to the surface prior to irradiation. Surface analysis techniques show that if cleaning is carried out below the damage threshold of the stone there is no modification to its physical or chemical structure.

Cleaning of limestone sculpture from Lincoln Cathedral and terracotta sculpture from the Victoria and Albert Museum shows laser cleaning to be more refined than conventional cleaning techniques and to have considerable advantages in the area of health and safety.
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INTRODUCTION

The formation of unsightly and damaging black encrustations on stone sculpture as a result of atmospheric pollution is a familiar problem. Traditional cleaning techniques, such as air-abrasives and water jets, have often proved successful in removing dirt but not without causing some damage to the surface of the stone beneath. The development of a precise and controlled technique which interacts only with the dirt layer is important for two main reasons:

(i) To restore the sculpture as near as possible to its original condition.

(ii) To increase the life of the sculpture.

The idea of using laser radiation to clean sculpture is not new. In the early 1970s tests were carried out in which a pulsed ruby laser was used to remove black encrustations from decaying marble sculpture. The tests were successful but at that time laser technology was expensive and largely undeveloped and conventional techniques provided a more practical and affordable solution.

Five years ago it was decided that the time was right to look once again at the feasibility of using lasers to clean polluted sculpture. During the past three years the interaction of laser radiation with polluted stone sculpture has been studied. This thesis describes work which has been carried out in that time, from the selection of the most suitable type of laser to the development of a practical laser cleaning tool.

Chapter one is an introduction and review chapter entitled The Decay and Conservation of Stone. The formation and properties of different types of stone are outlined. Processes of weathering and the effects of atmospheric pollution on stone are described. Reasons for cleaning stone sculpture are presented and a summary of conventional cleaning techniques and their limitations is given. Finally, previous work concerned with the use of lasers in the cleaning of polluted sculpture is reviewed.

Chapter two, A Comparative Study of Laser Cleaning, describes experiments which have been carried out to select the most suitable type of laser for the cleaning of polluted sculpture. The effects of different types of laser radiation, extending from the ultraviolet (248 nm) to the far infrared (10.6 μm), and xenon flashlamp radiation on
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various stone surfaces are described. Absorptivities of polluted and clean stone surfaces have been measured. Such measurements provide information useful in determining the suitability of different types of laser radiation.

Chapter three, *The Interaction of Laser Radiation with Stone*, describes the interaction of Nd:YAG laser radiation with polluted surfaces and the mechanisms by which material is removed. Techniques which clearly demonstrate the self-limiting nature of laser cleaning have been developed. These techniques are described and results presented for samples of limestone, sandstone and marble. Initial experiments using a transducer to monitor the longitudinal wave generated within stone during removal of material are also described.

Chapter four, *Laser Cleaning Methodology*, describes some of the practical techniques which have been adopted to improve the laser cleaning process. Surface analysis techniques have been used to evaluate the quality of cleaning achieved by laser. A brief review and some initial ideas for non-contact profiling of stone surfaces are also given.

Chapter five, *Laser Beam Delivery*, describes experiments which have been carried out to determine the most suitable type of laser beam delivery system for the laser cleaning of sculpture. This work has led to the development of a practical laser cleaning tool which is described.

Chapter six, *Conclusions and Further Work*, summarises the conclusions which have been made during the course of this work and suggests possible areas for future work. Examples of objects which have been cleaned by laser radiation are also presented.
CHAPTER 1

DECAY AND CONSERVATION OF STONE

1.1 Rock Types

The interior of the earth is known to consist of a number of distinct layers. These include a solid core with a radius of about 1400 Km, consisting mainly of a mixture of iron and nickel, which is surrounded by a liquid region about 2000 Km thick. This liquid is known as magma. The final layer is the outer crust which is not one continuous mass but rather a number of adjoining patches made up of three types of rock: igneous, sedimentary and metamorphic [1];

*Igneous* rocks are produced by the simple solidification of magma, either deep below the surface of the earth or at the surface as a result of volcanic activity. Granite, basalt, gabbro and porphyry are examples.

*Sedimentary* rocks are formed either by the accumulation of debris released by erosion, as with sandstone, or by the accumulation of dead plants or animals, as with limestone. The products of surface fragmentation are known as clastic, or fragmental rocks. Meteorological, plant and animal influences are constantly at work, releasing minute particles which surface moisture and wind are able to deposit elsewhere. Those rocks formed from the remains of plants and animals are known as organic rocks. Limestone deposited on the sea bed consists of calcite crystals formed over thousands of years from the skeletons of sea creatures. Other examples of sedimentary rocks are conglomerate, shale and dolomite.

*Metamorphic* rocks are formed by the action of heat and pressure on either igneous or sedimentary rocks. Examples are gneiss, slate, marble and diamond. Marble is metamorphosed limestone and diamond is formed by heating graphite to 2500 °C under a pressure exceeding $10^5$ atmospheres.

All rocks, known as *stone* if fabricated, are composed of one or more *minerals*. A mineral can be defined as a natural inorganic substance with a specific style of crystalline structure and definable chemical composition [2]. There exist more than
2000 species of minerals, one or more of which form the physical bulk of almost every stone used for building. Some of the important minerals include:

- calcite - calcium carbonate
- dolomite - double carbonate of calcium and magnesium
- feldspar - a group of rock forming alumino-silicates of potassium, sodium or calcium
- gypsum - hydrated calcium sulphate
- haematite - iron oxide
- quartz - commonest crystalline form of silica

To a large extent stone properties, such as colour and hardness, depend on the physical and chemical characteristics of the constituent minerals. The durability and aesthetic qualities of stone make it an ideal material for buildings and monuments. Stone has been used as a building material for over a thousand years but it is only during the last two centuries that the origin and nature of the different types have been scientifically studied and more fully understood. All stones, however, are not suitable for the same use or for use in the same location and there are many considerations which must be taken into account when choosing a particular stone for building. These include:

- The suitability of the stone for the type of building.
- The general architectural function of the stone - must the stone be strong enough to support a heavy load?
- The desired aesthetic effects - is surface texture important?
- Consideration of the local climatic and atmospheric conditions that the stone must withstand.

For a country as limited in size as Britain there exists a very large variety of stone for building [3]. Only one building stone was imported from abroad in large quantities and over hundreds of years: a light creamy-yellow limestone from Caen in Normandy which was used in the building of Henry III's Westminster Abbey and made a large contribution to cathedrals at Rochester, Canterbury and Winchester. Stones used widely for building in Britain can be divided into five main groups: granites, slates, sandstones, limestones and marbles;
Granite has been widely used in Britain for building and ornamental purposes. The term granite is often used to describe coarse-grained igneous rocks which contain free quartz and whose other main constituent minerals are feldspar and mica [2]. Granite has a wide range of colour - from the greys and whites of Cornwall and Aberdeenshire to the pinks of Shap and Peterhead - and is well known for its hardwearing qualities.

Slate occurs throughout Britain and is a popular choice as an external cladding material, particularly on roofs. A true slate is defined as a metamorphosed argillaceous sedimentary rock and is to be found in Wales, Cornwall and parts of Scotland. The Lakeland Green Slates are actually derived from fine volcanic ash and are to be found in areas of the Lake District. Slate is impervious to water and usually exists in a laminated condition which means that it can quite easily be split into thin layers making it highly suitable for roofing.

Sandstone is a sedimentary rock consisting mainly of grains of quartz or silica, sometimes with the addition of small quantities of feldspar, mica or some other mineral, and always a cementing material known as the matrix of the stone. The matrix varies considerably and essentially determines the strength, durability and colour of the stone. The strongest cement is silica, the weakest clay, with calcite, dolomite and iron oxides in between. The wide range of colours of sandstone, from dull crimson and pale buff to greenish brown and blue-grey, together with its strength and durability have made it popular as a building material, particularly in Scotland and the western and northern counties of England. Siliceous sandstones are chemically inert and are able to withstand rigorous weather conditions. Red sandstones have been used in the present century in the building of Coventry and Liverpool Cathedrals.

Limestone is a sedimentary rock consisting mainly of calcium carbonate in the form of the mineral calcite. Many limestones also contain a proportion of dolomite and some contain sand or clay. A 'pure' limestone is white or pale grey but small amounts of carbonaceous matter or iron oxides may be sufficient to colour the stone. Limestone is a rarity in most of Wales and Scotland but England has extensive deposits, particularly on the Jurassic limestone belt which stretches across the country from Dorset to the Yorkshire coast. Limestone is able to withstand severe frosts and driving rain does little harm since stone walls are able to quickly dry out. However, limestone is not chemically inert and sulphur released into the atmosphere, once activated by rainwater, can be corrosive to the surface of the stone. The oolitic limestones are generally considered to be visually the finest of all the English stones [3] and were used in the building of the cathedrals at Lincoln, Peterborough, Ely, Oxford, Wells and London's
St. Paul's. The ooliths are small spherical grains, the size of a pin head or less, with an internal structure of calcite. Calcite also acts as the matrix, holding the ooliths together. Portland stone, a chalky white oolitic limestone, has been used extensively in southern and western English cities, particularly in central London ever since it was first used in the construction of St. Paul's Cathedral.

*Marble* is metamorphosed limestone. It is composed of crystals of calcite, all fossils having disappeared, and if no other material is present is pure white. The presence of impurities or other minerals in cracks, an effect known as veining, may provide some colour. Most of the true marbles which are used in Britain are imported from countries including Belgium, Norway, Italy and France. Marble has a fine-grained, compact, even structure and is relatively soft when freshly quarried making it easy to carve. Its ability to take a high polish made it a popular choice for decorative stonework, but meant that it could only be used internally in Britain. Exposed to the poor climate and polluted atmosphere, marble would quickly lose its polish and its appeal. The interior of Westminster Cathedral has many fine examples of different marbles and mosaics.

No two blocks of stone, even if quarried next to each other, have exactly the same physical and chemical composition and internal structure. The differences may be minute and of no practical importance but they may also be substantial, making it necessary to carefully consider the most suitable use for each block. Stone must, therefore, be regarded as a material of great variety requiring individual treatment in order to use it to its full potential.

### 1.2 The Decay of Stone

The prolonged exposure of stone buildings and monuments to the environment will eventually lead to deterioration of the stone. This can take the form of a change in appearance, strength, size or chemical behaviour of the material and may apply to individual sections or to the structure as a whole. The factors which can affect the stone include [4]:

- Chemical attack, i.e. etching and dissolution, of alkaline stones (particularly limestones) by acidic solutions either from natural (carbon dioxide, volcanic gases, rain water) or man-made (combustion of fossil fuels) sources.
Chapter 1: Decay and Conservation of Stone

- Mechanical disruption caused by forces generated within pores and cracks of the stone by freezing of water, growth of crystals, or corrosion of metals or minerals (e.g. pyrites).

- Alteration of the appearance by movement of coloured material into stone from adjacent objects (e.g. rust and copper staining), or alteration to the original colour or texture by leaching from the stone of one or more of its components, or by the roughening of a polished surface.

- Abrasion and cracking resulting from airborne particles, seismic shocks, vibrations from traffic and human contact.

- Chemical and mechanical disruption of the stone and changes to its appearance resulting from plant growths such as fungi, algae and mosses, and the activities of higher organisms such as pigeons.

- Exfoliation and disintegration due to poor design and construction, such as the use of a too strong mortar.

- Mechanical and chemical damage resulting from poor restoration with substances that are unstable or whose physical properties, such as thermal expansivity, do not match those of the stone.

- Alteration to the appearance of the stone by unsightly surface deposits of soot, dirt, grease and paint.

The dominant form of stone decay in a particular location will be dependent on the physical and chemical properties of the stone being considered and on the environmental conditions to which it is exposed. Increased levels of atmospheric pollution have been shown to lead to accelerated decay of stone monuments in urban areas [5]. It has been suggested that in the past 75 years air pollution has been responsible for almost as much damage to works of art as the previous 500 years of ordinary weathering [6]. Examples of ancient stone monuments in urban areas which have suffered severely from accelerated weathering include the Parthenon in Athens [7], Cologne Cathedral [8], the Taj Mahal in Agra [9], St. Paul's Cathedral in London [10] and the many Venetian marble buildings [11]. This section describes the nature and mechanisms of the main causes of stone decay, both those attributed to ordinary
weathering (wind, rain, heat, plants, animals etc.) and those resulting from atmospheric pollution.

### 1.2.1 Stone Weathering

The natural deterioration of stone is a result of physical, chemical, mechanical and biological processes which are principally due to changes between the initial formation environment of the rock and the new environment to which it becomes exposed [4]. The durability of stone depends to a large extent on: (i) its internal structure and petrographic composition and (ii) the environment to which it is exposed. The true mechanism by which a stone will decay is very complicated and probably not fully understood. It is known, however, that deterioration can occur through several mechanisms which may occur independently or co-operatively, consecutively or simultaneously [12]. It is, therefore, necessary to make certain assumptions separately in order to build up a model which can be used to explain and predict the behaviour of a particular stone in a known environment.

Water plays a very important role in the deterioration process. The penetration of moisture into a stone body is made possible by the porous nature of stone. A porous body is formed from solid particles which are arranged in a structure with empty spaces called pores [4]. Porosity can be defined as the ratio of the total volume of the pores to the total volume of the stone. The porosity and nature of the pores is dependent on the type of stone and on its exposure to weathering before and after its incorporation in a building or monument. Porosity can vary between 0.1% (for some slates, quartzite and basalt) and 30% (for some shales); limestones and sandstones have typical values in the range 5 - 25% [13]. The size of the pores may be very small, less than 0.01 µm radius (micropores), or as large as 100 µm radius (macropores). The movement of moisture within a stone body is made possible if the pores are interconnected.

The porosity of stone can be very susceptible to temperature variations. For example, the porosity of certain types of marble have been found to increase by as much as 40 - 50% of the original material when they are subjected to variations in temperature of 50 °C [14]. The increase in porosity has been attributed to the marked anisotropy of calcite crystals; the dependence of the thermal expansion coefficient on direction means that an increase in temperature causes the crystal to expand in one direction, but contract in another [15]. This kind of movement can lead to internal cleavage of
crystals and detachment of one crystal from another. A stone which has experienced an increase in porosity may suffer accelerated rates of decay since conditions are more favourable for the circulation of water containing soluble salts and the formation of microcracks which allows the penetration of air pollutants.

### 1.2.1.1 Moisture Travel and Evaporation

The presence of water in a stone body can be very harmful in that it allows: (i) the chemical reaction of stone constituents, (ii) the transportation, migration and crystallisation of soluble salts and (iii) enhanced chemical attack on the stone by dissolving airborne atmospheric pollutants in droplets which can remain in contact with the stone for a long time. Not only does water make chemical action possible but it can also lead to the generation of internal stresses [4]. Forces sufficient to cause disruption to the stone can be generated by the expansion of water within the pores during heating and as a result of its increase in volume during freezing.

Water reaches stone by a number of routes including:

(i) Rainfall; the walls of a building which are exposed to wind and rainwater are subjected more to water penetration.

(ii) Rising damp by capillary absorption.

(iii) Condensation; when water vapour reaches a maximum concentration for a given temperature and comes into contact with a sufficiently cold surface, a thin layer of water forms on the surface itself.

(iv) Water vapour, which is nearly always present in the atmosphere, penetrates into the pores. A specific quantity, which is dependent on the relative humidity of the air, is held in the stone.

Deterioration processes occur most commonly when water evaporates, i.e. during the drying phase. Evaporation of water from porous materials takes place at the surface and depends on several factors:
(i) The supply of moisture from the interior; the evaporation of water molecules on the surface causes a migration of water to the surface which depends on the structure of the material.

(ii) The temperature of the ambient air; the rate of evaporation increases as temperature increases.

(iii) The ventilation on the surface; the rate of evaporation increases as the velocity of air passing the drying surface increases [4].

When a saturated material dries in the presence of high relative humidity and no ventilation, the rate of evaporation is low and the surface remains wetted. If there is ventilation the evaporation rate increases and provided water can move to the surface quickly enough to compensate for the loss by evaporation, the surface will remain wetted and evaporation will proceed at a constant rate. When the amount of water brought to the surface is insufficient to keep the surface wetted the evaporation rate decreases. Hence, in a dense material where the water cannot move easily, the surface may dry before all the pores have emptied and at a point below the surface the material may still be saturated. The evaporation rate decreases rapidly as the water front retreats into the material.

Water in stone is transported through capillaries. A capillary system with open channels, interconnected large pores and isolated vugs is shown in figure 1.1.

![Figure 1.1: Hypothetical pore system.](image)
A vug is a cavity in the rock, often lined with a crystalline encrustation. The pores may be filled with fluid, partly filled, in which case air pockets will be present, or almost completely empty with an adsorbed coating along the walls measuring a few molecules in thickness [13]. The transport of water through a porous body is by capillary suction [4] and depends on the capillary structure. The cause of capillary suction is the attraction of water towards the walls of the pores. Most porous bodies are composed of carbonates, silicates or oxides which contain polar atoms (oxygen) or groups of atoms which show a strong electrostatic attraction for polar molecules, such as water, as shown in figure 1.2. The water front which moves inside the pore adopts the shape of the meniscus shown in figure 1.3 because the centre of the water surface is pulled inwards by the attraction of other water molecules, while close to the pore surface the attraction of the pore walls takes over.

Figure 1.2: Water attraction by a pore wall.

Figure 1.3: Meniscus formed by a water front inside a narrow pore.
Transport of water can occur both vertically and horizontally. Vertical transport occurs when water enters the stone from above, e.g. through a leaking gutter, or rises through the stone from the ground as a result of accumulation of water at the base. The smaller the pore diameter the larger the capillary force. For pores which are sufficiently small the capillary action is sufficient to overcome gravity and the water rises. The transport of water through capillaries can lead to the diffusion and precipitation of soluble salts. These salts have various origins: (i) they may have been originally present in the stone, (ii) they can be derived from decomposition of the stone or (iii) they may be derived from external sources such as jointing materials, soil, atmosphere and previous attempts at cleaning and preservation.

1.2.1.2 Efflorescence

Evaporation of water containing dissolved salts gives rise to an increase in salt concentration and subsequent crystallisation. Crystallisation of soluble salts can take place at different points in the pores depending on the solubility of the salts and the rate of water evaporation. If the evaporation rate is less than the rate at which water migrates to the surface from within the stone then crystallisation will occur at the surface. The formation of unsightly blotches, patches and margins of white salts on the surface of stone is termed efflorescence.

Figure 1.4: Efflorescence; a) Wetting phase: water on surface. b) Drying phase: evaporation of water and crystallisation of salts.
When efflorescence occurs salts are brought to the surface in solution during the wetting phase and most of the evaporation takes place during the drying phase, as shown in figure 1.4. Salts on the surface are an indication of salt migration and the upper limits of moisture travel but generally do no harm to the stone. The most common salts occurring in efflorescence are sulphates, nitrates, chlorides and carbonates of alkali metals and magnesium. Sulphates are mainly derived from ground water, sea water or atmospheric pollution; chlorides are mainly of maritime origin; nitrates have sources in decomposing organic material, agricultural ground and atmospheric pollution; carbonates are major constituents of many building stones.

1.2.1.3 Subflorescence

If the evaporation rate of moisture from the exposed surface is greater than the rate of replenishment from the interior then the surface becomes dry and most of the evaporation takes place from within the stone [4]. Crystallisation of soluble salts will then occur within the pores. This phenomenon is called *subflorescence* and is shown in figure 1.5.

Crystals form and grow in the pores and cracks along the interface between the wet and dry zones at a distance d below the surface. As the crystals grow they exert forces on the stone causing the dry zone to separate or crumble. Subflorescence is an important cause of the decay of building stones.
1.2.1.4 Hydration Pressure

There exist crystals in which some water molecules occupy well-defined positions in the crystal structure. These salts are said to be hydrated. An example is gypsum, CaSO₄·2H₂O, which is hydrated calcium sulphate. Changes in the temperature and humidity of the atmosphere will cause these salts to adopt a more stable form. Loss of water of crystallisation and hydration can take place within the capillaries. The associated volume change of the crystal can lead to strong forces on the walls of the individual pores [16].

Monuments in urban areas, exposed to a semi-humid moderate climate, may be saturated with salts from polluted air, mortar and ground water [13]. An increase in relative humidity leads to hydration. This absorption of water increases the volume of the salts, thereby applying pressure to the pore walls. If this hydration pressure exceeds the resistance of the pore walls they are broken, increasing the porosity and making the stone more susceptible to the action of humidity and salts.

1.2.1.5 Frost Action

The vulnerability of a particular stone to damage by frost depends on several factors including its mineralogical properties, porosity and location. Damage can take many forms including deep cracking and exfoliation. Variations in temperature about the freezing point produce more damage in stone than continuous freezing. In countries in Northern Europe stone walls remain frozen for a large part of the year. In countries further south, e.g. Switzerland, large temperature variations can occur daily. Freeze-thaw cycles are more frequent, thereby increasing the susceptibility of stone to frost damage. Damage to stone can be explained by several mechanisms including [13]: (i) the volume increase of water to ice and (ii) the displacement of pore water away from the advancing frost. When water freezes with a normal expansion of about 10%, pressure develops if freezing occurs within a confined space. If sufficient water is present in the pore system freezing can result in the generation of forces capable of disrupting the stone. Hydraulic pressure can be generated within the stone during the initial freezing, whereby still unfrozen water is displaced away from the advancing front of frost towards a pore wall.
1.2.1.6 Differential Thermal Expansion of Salts

Disruption of stone can occur if there exist considerable differences in the thermal expansion of salts trapped in the pores. Halite (NaCl), for example, expands 0.5% by volume for a temperature rise from freezing to 60 °C whereas granite expands less than 0.2% [13]. The forces exerted on pore walls as a result of salt expansion may be sufficient to cause damage to the stone.

1.2.1.7 Decay by Plants and Animals

Plants and animals can attack stone by both mechanical and chemical action. The action of higher plants may be both mechanical and chemical, whereas bacteria, the lowest kind of life, attack by chemical action only.

Microbiological attack is by chemical secretion and photosynthetic activity. Certain types of bacteria bring about and accelerate chemical reactions. The biological degradation of carbonate rocks has been attributed primarily to the action of nitrificating bacteria [17] which can produce the reaction:

\[ 2\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4 + 4\text{O}_2 \rightarrow \text{Ca(NO}_3)_2 + \text{CaSO}_4 + 2\text{CO}_2 + 4\text{H}_2\text{O} \]

This reaction leads to the presence of calcium nitrate and a small amount of gypsum on limestone walls. Fungi attack silicate minerals and carbonates by the secretion of carbonic, nitric, sulphuric and some weaker acids. Lichens growing amongst translucent minerals bring about discoloured patches of brown and pink. Lichens can damage stone by secretion of acids and by water retention; the rough surface and spongy nature retain water for a long time which keeps the stone surface moist underneath. This may contribute to damage later as the stone is unable to rid itself of moisture. The most intense biological activity is usually found just above the soil level.

Plant roots can damage stone by mechanical action. Roots are able to wedge themselves within cracks in the stone and weak mortar joints and exert forces which may result in further damage.

Birds often inhabit sheltered parts of buildings. Large quantities of bird droppings contain some phosphoric and nitric acids which etch stone or react with carbonates to form calcium phosphates and nitrates [13].
1.2.1.8 Summary

Moisture plays an important role in the decay of stone, both as a means of transport and as a disruptive agent. Expansion of water in pores when heated and the volume increase associated with the transformation of water to ice can lead to the disruption of stone. Moisture can move both vertically and horizontally within stone by capillary action.

Salts which can be derived from stone weathering, polluted air or ground moisture are able to move within stone by diffusion and by capillary action. Surface efflorescence, subflorescence, salt crystallisation and salt hydration in stone pores can produce pressures sufficient to cause damage to the stone. Differential thermal expansion of salts trapped within pores is considered to be less important [13]. Plants and animals are also able to attack stone, by both mechanical and chemical means.

1.2.2 Effects of Atmospheric Pollution on Stone

The rapid expansion of urban areas and the concentration of industry during the past hundred years has led to an increase in air pollutants which has accelerated the rate of decay of many urban stone monuments [5, 7-11]. A pollutant is a substance which produces a change in the composition of normal air. This may include almost any natural or artificial matter which can be airborne [18]. Pollutants exist as solid particles, liquid droplets, gases or as a mixture of different states. They can be emitted directly from an identifiable source or produced in the air by the interaction of two other pollutants or by reaction with normal atmospheric constituents. Pollutants relevant to stone decay include: carbon dioxide, nitrogen oxides, hydrogen fluoride, hydrogen chloride, ammonia, hydrogen sulphide, ozone, particulate matter and sulphur oxides.

Aerosols are defined as mixtures of sufficiently fine dispersed particles with air [4]. Particles can be solid or liquid droplets and are produced either by disintegration of matter (e.g. dust storms, sea spray) or by condensation from the gas phase (e.g. smokes produced by industry). Particle size ranges from a single molecule to a raindrop. Aerosols formed by liquid droplets are often called mist. Aerosols formed by solid particles are often called dust. In general, atmospheric aerosols are composed of a complex mixture of solid and liquid particles with each particle a mixture of solid and liquid substances.
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The removal of pollutants from the atmosphere occurs continuously to prevent the amount of toxic substances from reaching a level which would make our atmosphere unliveable. There are several mechanisms of natural removal [19]:

1. Removal of aerosols:
   - Fallout due to gravity as dust or soot.
   - Impact and capture of particles on objects at the earth's surface.
   - Washing out by precipitation.

2. Removal of gases:
   - Escape into space of light gases such as hydrogen and carbon monoxide.
   - Absorption, decomposition or both at the earth's surface by vegetation and mineral weathering or hydrolysis.
   - Decomposition in the atmosphere by reactions resulting in the formation of aerosols or other gases (formation of smog).
   - Washout by precipitation.

Washout by precipitation is thought to be the most important process by which pollutants are removed from the atmosphere and concentrated into small volumes of liquid. On a local scale dry deposition can be dominant, particularly in heavily polluted areas.

The composition of clean, dry air is: 78.09% nitrogen, 20.94% oxygen, 0.93% argon, 0.032% carbon dioxide and traces of neon, helium, krypton, xenon and methane which total about 0.004%. Air also contains a large number of other trace gases such as carbon monoxide, hydrogen, nitrogen dioxide, sulphur dioxide and many hydrocarbons which occur naturally but are present in very low concentrations [4]. Most substances known as pollutants are present naturally and are only increased significantly by the activity of man. The water vapour content of the atmosphere is highly variable, between 200 ppm (parts per million) in arid regions and 60 000 ppm in a warm, humid climate and is very dependent on geographical location (proximity of water sources, wind direction and ambient air temperature [18]). The presence of water is often necessary if certain pollutants are to attack a stone surface. The activity of man affects the quality of the atmosphere, particularly in dense urban areas and near to large emission sources such as power stations. Considering the world as a whole, the total mass of pollutants emitted by nature is thought to exceed that emitted by man-made
sources, although it has been predicted that by the year 2000 man-made and natural sources will be approximately equal [20]. For sulphur dioxide, however, man-made sources already exceed natural sources with about 60% thought to be derived from man-made sources [21]. In urban areas the situation is more serious since man-made emissions can be several orders of magnitude higher than natural sources which gives rise to accelerated rates of stone decay.

1.2.2.1 Pollutant Types

This section describes atmospheric pollutants which contribute directly, forming aggressive substances, or indirectly, forming intermediate compounds, to the deterioration of stone buildings and monuments.

Carbon Dioxide

Carbon dioxide (CO$_2$) is a natural constituent of the atmosphere. Plant life has a considerable effect on the CO$_2$ concentration at the surface of the earth. During daylight photosynthesis results in a decrease of the CO$_2$ concentration due to assimilation by plants. At night time photosynthesis is unable to continue but decomposition and respiration of organic matter does proceed, replacing the lost CO$_2$. Since about 1900 the average CO$_2$ concentration in the northern hemisphere has been increasing at a constant rate; the increase has been attributed to the burning of fossil fuels [22]. Between 1891 and 1964 the average CO$_2$ concentration in Paris increased from 320 ppm to 351 ppm [23]. Both the CO$_2$ concentration and its rate of change are increasing in Paris, a trend which is thought to be typical of many urban areas throughout the world. An increase in CO$_2$ concentration will lead to a rise in the surface temperature of the earth via the greenhouse effect, and a subsequent increase in the water vapour content of the atmosphere.

The presence of CO$_2$ in the atmosphere can lead to the decay of carbonate-containing stones [4]: limestones, marbles [9] and some sandstones. CO$_2$ in air dissolves in rainwater initially forming CO$_2$.H$_2$O via the reaction:

$$\text{CO}_2\text{gas} + \text{H}_2\text{O}_{\text{liquid}} \rightarrow (\text{CO}_2 \cdot \text{H}_2\text{O})_{\text{liquid}}$$

CO$_2$.H$_2$O in water dissociates into HCO$_3^-$ and CO$_3^{2-}$ via:

$$\text{CO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$$
and

\[ \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \]

The weak carbonic acid solution formed by dissolution of CO$_2$ in rainwater, which may have a pH of as low as 5.65 [9], dissolves the calcium and magnesium carbonates in limestone, dolomite, marble, lime mortars and plaster by reacting to form the much more soluble calcium and magnesium bicarbonates:

\[ \text{CaCO}_3 + \text{CO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{Ca(HCO}_3)_2 \]

\[ \text{MgCO}_3 + \text{CO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{Mg(HCO}_3)_2 \]

An increase in the CO$_2$ concentration results in increased production of bicarbonates and, hence, further damage to the stone. A rise in temperature of a calcium bicarbonate solution on a marble surface can lead to the evaporation of CO$_2$ and the recrystallisation of calcite via the reaction:

\[ \text{Ca(HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

However, the calcite formed consists of larger crystals and has a porous structure compared to the original calcite which is microcrystalline and non-porous. This increase in porosity can lead to accelerated decay since acidic solutions and soluble salts are able to penetrate more deeply into the stone.

Calcareous sandstones are susceptible to weakly acidic rainwater since the carbonate which cements silica grains together is attacked, destroying the structure of the stone surface.

**Carbon Monoxide**

Carbon monoxide (CO) is produced in large quantities by combustion processes, when insufficient oxygen is present for complete oxidation to CO$_2$:

\[ 2\text{C} + \text{O}_2 \rightarrow 2\text{CO} \]

However, 75% of the CO present in the atmosphere is derived from natural sources [4]: natural gases, forest fires, volcanoes and bacterial action in the ocean. CO is not corrosive to stone but can pose a threat indirectly, as a source of CO$_2$ in the atmosphere and as a catalyst in the oxidation of sulphur dioxide.
Nitrogen Oxides

Nitrogen is a very stable gas and reacts only under conditions of high temperature or pressure such as in a combustion process. Nitrous oxide (N$_2$O), nitric oxide (NO) and nitrogen dioxide (NO$_2$) are the only oxides of nitrogen to be found in the atmosphere. N$_2$O is produced mainly by combustion and as a result of soil bacteria activity. NO is produced by combustion engines, by lightning and in soils [4], with concentrations in the atmosphere varying between 100 ppb (parts per billion) in polluted areas and 0.01 ppb in remote marine areas. The high temperatures in a combustion zone can lead to the reaction of nitrogen with oxygen in the air to form NO via the reaction:

\[
N_2 + O_2 \leftrightarrow 2NO
\]

In exhaust gases some NO is oxidised to NO$_2$:

\[
2NO + O_2 \leftrightarrow 2NO_2
\]

In air NO is more susceptible to oxidation by ozone than by oxygen:

\[
NO + O_3 \rightarrow NO_2 + O_2
\]

Oxidation of nitrogen oxides in the atmosphere can lead to the formation of nitric acid [18] which can have a corrosive effect on stone. The most likely mechanism of formation of nitric acid is:

(i) Oxidation of NO$_2$ to NO$_3$ in the presence of ozone: \( NO_2 + O_3 \rightarrow NO_3 + O_2 \)

(ii) Formation of N$_2$O$_5$: \( NO_2 + NO_3 \rightarrow N_2O_5 \)

(iii) Hydration to nitric acid: \( N_2O_3 + H_2O \rightarrow 2HNO_3 \)

The presence of nitric acid vapour has not yet been detected in the general urban atmosphere although this result may be a consequence of the inadequate sensitivity of present detection methods. However, both organic and inorganic nitrates have been found [18]. The damaging effect of nitrates on stone is thought to be due to their action as soluble salts within the stone [4]. In regions where nitric acid does occur, in smog, for example, where hydration and catalytic oxidation give rise to the complete conversion of NO$_2$, its prolonged action on stone can lead to deterioration by the conversion of substances into nitrates [24]. This action can be particularly corrosive on
carbonate stones since the calcium carbonate is converted to calcium nitrate which will go into solution [9]:

$$\text{CaCO}_3 + 2\text{HNO}_3 \rightarrow \text{Ca(NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2$$

In most polluted areas the removal of nitrates from the atmosphere contributes to the acidity of precipitation. In the eastern United States, for example, where regional pH values have reached levels of below four [9], the concentration of nitrates accounts for 30 - 40% of the acidity in precipitation.

**Ammonia**

Ammonia (NH₃) is an alkaline gas which reacts with acidic pollutant gases to form ammonium salts. The main source of NH₃ is the decomposition of amino acids as a result of bacterial activity. NH₃ is not thought to have any direct effect on stone but it can aid deterioration indirectly by its role in the aqueous oxidation of sulphur dioxide (SO₂); the absorption of NH₃ can increase the pH to a range (4-5) where oxidation of SO₂ in the presence of catalysts proceeds more readily [25]. Removal of NH₃ from the atmosphere can take place by incorporation of gaseous NH₃ or particulate ammonium ions into rain droplets followed by wet deposition to the ground.

**Fluorine and Hydrogen Fluoride**

Fluorine (F₂) emitted into the atmosphere is very reactive and quickly forms compounds. Hydrogen fluoride (HF) is frequently observed since it results from certain industrial operations including the manufacture of glass, brick and some fertilisers, as well as the combustion of coal in which fluoride is present [4]. HF can react with calcareous stones forming fluorite (CaF₂) which is stable and insoluble:

$$2\text{HF} + \text{CaO} (\text{CaCO}_3) \rightarrow \text{CaF}_2 + \text{H}_2\text{O}$$

Fluoride levels have been measured at Cologne Cathedral [8]. The annual mean uptake rate, defined as the amount of substance absorbed by a unit area of stone in a unit time for fluoride was in the range 0.41 - 1.24 mg m⁻² day⁻¹, compared to 85.4 - 111.5 mg m⁻² day⁻¹ for SO₂.

The effects of fluorides on siliceous and calcareous stones have been studied by exposing stone samples to an artificial HF atmosphere. The exposure of siliceous stone surfaces led to two types of deterioration [26]: (i) nucleation and growth of new crystalline phases, such as silicon tetrafluoride and (ii) formation of fissures and
microcracks, partly due to stresses generated by the difference in volume between the initial and new crystalline phases. These alterations give rise to a lack of cohesion among the components of the stone, thereby increasing susceptibility to other erosion phenomena. Exposure of calcareous stone to HF led to the formation of a thin whitish layer composed almost exclusively of fluorite and silica [27]. Formation of microcracks and fissures, and the nucleation and growth of new phases was observed. The increase in surface area of the stone brought about by the formation of fluorite leads to accelerated decay by other mechanisms.

Chlorine and Hydrogen Chloride
Chlorine (Cl₂) is used widely in the chemical and plastics industries and in water and sewage treatment plants. Reactions in the atmosphere can lead to the production of very low concentrations of Cl₂ [4]; sodium chloride can react with nitrogen dioxide to form nitrosyl chloride (NOCI):

\[
\text{NaCl} + 2\text{NO}_2 \rightarrow \text{NOCI} + \text{NaNO}_3
\]

which may decompose photochemically to form Cl₂ and nitric oxide according to:

\[
2\text{NOCI} \rightarrow 2\text{NO} + \text{Cl}_2
\]

Hydrogen chloride (HCl) is a common air pollutant, present in higher concentrations than elemental chlorine. The abundance of HCl in the atmosphere was measured in Venice during 1972 and 1973 [11]. Mean monthly concentrations were found to vary between 14 μgm⁻³ (July 1972) and 50 μgm⁻³ (May 1973). HCl is emitted from industrial sources, such as hydrochloric acid manufacturing plants, and from the combustion of coal, paper and chlorine containing plastics. Gaseous chloride particles found in the atmosphere away from urban sources are thought to be partly the result of reactions between sea-salt particles and sulphuric acid formed by slow oxidation of atmospheric sulphur dioxide [28]:

\[
2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow 2\text{HCl} + \text{Na}_2\text{SO}_4
\]

Evidence that this reaction does proceed is the presence of thenardite (Na₂SO₄), which has been discovered in salt efflorescences in buildings in Venice [29].

Hydrochloric acid can have a damaging effect on stone building materials, particularly on carbonate stones. The deterioration of samples of green antique marble in Venice
has been partly attributed to the formation of antarcticite (CaCl₂.6H₂O) by the reaction of calcite with atmospheric HCl, according to [30]:

\[
CaCO_3 + 2HCl \rightarrow CaCl_2 \cdot 6H_2O + H_2CO_3
\]

Sodium chloride can be transported into stone in solution and subsequent crystallisation causes mechanical stresses which may be sufficient to damage the stone.

**Sulphur Oxides**

Sulphur is present in the atmosphere in gaseous compounds, mainly sulphur dioxide (SO₂), sulphur trioxide (SO₃) and hydrogen sulphide (H₂S). SO₂ is considered to be the single most important pollutant because of its potential conversion to sulphuric acid which readily attacks stone, particularly carbonate-containing stone. The combustion of fossil fuels produces both oxides of sulphur with SO₂ the most abundant form:

\[
S + O_2 \leftrightarrow SO_2
\]

\[
2SO_2 + O_2 \leftrightarrow 2SO_3
\]

The amount of sulphur trioxide produced is usually between 1 and 10% of the total sulphur oxides emitted into the atmosphere. If the water vapour content of the atmosphere is very low SO₃ may exist in gaseous form, but more usually the water vapour content is sufficient for SO₃ to form droplets of sulphuric acid according to:

\[
SO_3 + H_2O \rightarrow H_2SO_4
\]

Coal typically contains 1 - 3% sulphur which is present as iron pyrites, FeS₂, organic compounds and sulphates. Since industrialisation sulphur pollution has become a large scale problem. For industrialised countries the mean consumption of coal is about one ton per person per year (including industry) [13]; combustion of one ton of coal can emit as much as 52 Kg of SO₂ into the atmosphere [20]. Crude oil contains varying amounts of sulphur, typically between 0.75 and 2.5%, while natural gas normally has a lower sulphur content.

Measurements made in Venice [11] and Cologne [8] have shown that atmospheric SO₂ concentrations tend to be seasonal with a maximum during the colder winter months when heating of homes and offices increases. In December 1972 the mean monthly
concentration of SO$_2$ in Venice was about 360 $\mu$g m$^{-3}$, whereas the figure for June 1972 was about 20 $\mu$g m$^{-3}$. SO$_2$ is removed from the atmosphere by a number of mechanisms:

(i) Incorporation into clouds and wash out by rain.

(ii) Direct deposition onto stone and vegetation.

(iii) Conversion into sulphuric acid in the presence of nitrogen oxides, hydrocarbons and trace metals.

(iv) In moist atmospheres SO$_2$ can react with ammonia to form ammonium sulphate.

The incorporation of SO$_2$ in cloud droplets and removal by precipitation can lead to the formation of acid precipitation which has been observed for a long time in Europe, and also in the United States and Canada. High sulphate levels resulting from SO$_2$ emissions can cause the acidity of precipitation to fall below 5.65 (the equilibrium pH value with atmospheric carbon dioxide) [9].

Carbonate stones exposed directly to rainfall are especially vulnerable to acidic attack and subsequent stone dissolution. Sulphuric acid will react with calcium carbonate to form the much more soluble calcium sulphate which is washed away during periods of rain. The reaction proceeds as [7]:

$$\text{CaCO}_3 \text{solid} + \text{SO}_2 \text{gas} + 1/2 \text{O}_2 \text{gas} + \text{H}_2\text{O} \text{liquid} \rightarrow \text{CaCO}_3 \text{solid} + \text{H}_2\text{SO}_4 \text{aqueous}$$

$$\text{CaCO}_3 \text{solid} + \text{H}_2\text{SO}_4 \text{aqueous} \rightarrow \text{CaSO}_4 \text{aqueous} + \text{H}_2\text{CO}_3 \text{aqueous}$$

$$\text{CaSO}_4 \text{aqueous} + \text{H}_2\text{CO}_3 \text{aqueous} \rightarrow \text{CaSO}_4 \text{aqueous} + \text{CO}_2 \text{gas} + \text{H}_2\text{O} \text{liquid}$$

Direct exposure of a building to acid rain can, therefore, lead to damage, often in the form of local dissolution of high reliefs, exfoliations and detachment of pieces of stone.

On parts of a building which are sheltered from direct rainfall, attack by SO$_2$ occurs via a different route [7, 32-34]. SO$_2$ which has accumulated on the stone surface is oxidised to SO$_3$ by catalytic action due to surface impurities such as iron (III) oxide (Fe$_2$O$_3$), to calcium carbonate itself, to calcium sulphate in solution, to humidity and to
sulphur oxidising bacteria. In the presence of moisture, reaction between SO$_3$ and calcium carbonate leads to the formation of a gypsum (CaSO$_4$.2H$_2$O) crust. Thus, sulphation consists of two consecutive reactions which can be represented by:

\[
\text{SO}_2 \text{gas} + \text{air} + \text{catalyst} \rightarrow \text{SO}_3 \text{gas}
\]

and

\[
\text{CaCO}_3 \text{solid} + \text{SO}_3 \text{gas} + 2\text{H}_2\text{O}_\text{gas} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O}_\text{solid} + \text{CO}_2 \text{gas}
\]

Measurements made on marble in statues and monuments at the Acropolis have revealed that surfaces which are sheltered from rain water consist of 85 - 97% CaSO$_4$.2H$_2$O, the remainder being CaSO$_3$.2H$_2$O (resulting from non-oxidised SO$_2$) and calcium carbonate. The thickness of gypsum crusts varied from 0.1 - 1.5 cm. Some gypsum in solution is able to penetrate into the stone through cracks, cleavage and intercrystalline boundary planes. Crystallisation of gypsum within the stone can create pressures capable of splitting the cement into fragments, thereby weakening the structure of the stone [31]. The depth to which gypsum penetrates, the zone of weathering, depends on the porosity characteristics of the stone [9]. Georgia marble, for example, is relatively compact and contains bands of fine-grained minerals whereas a Carrara-type marble is more porous and lacks the fine-grained minerals in the interstices. Thus, a typical zone of weathering of a Carrara marble (4 mm) is thicker than that of a Georgia marble (0.5 mm). Details of the surface relief of the stone are preserved by the gypsum film but are lost on the gypsum/stone interface. Removal of the film, either by cracking induced by sudden fluctuations in temperature and humidity or by washing can, therefore, result in the loss of detail from stone surfaces.

The effect of sulphate attack on silicate rocks is not fully understood but is thought to enhance the process of kaolinisation [13] in which leaching unlocks and frees the metal cations (calcium, sodium, potassium, magnesium) from the crystal lattice of the silicate mineral and exposes the gaps left to hydration.

**Hydrogen Sulphide**

Hydrogen sulphide (H$_2$S) is the most reduced form of sulphur. The unpleasant smelling gas is produced by many biological processes on land, in marshes and in the oceans. Man-made sources are thought to account for approximately 3% of the total emitted into the atmosphere, with contributions from the rayon and oil-refining industries [4]. H$_2$S concentrations of between 0.1 and 1 $\mu$gm$^{-3}$ have been recorded in urban areas [35]. The transformation of H$_2$S into sulphuric acid by certain bacteria can be harmful to limestones and marbles.
Ozone
Ozone ($O_3$) is an important constituent of the atmosphere in that it strongly absorbs the energetic portion of the ultraviolet radiation received from the sun, thereby preventing serious damage to living tissues. Ozone formation is strongly influenced by nitrogen oxides produced by man's activities [36]. In polluted environments nitric oxide and nitrogen dioxide act as catalysts in the production of ozone by photochemical oxidation of the unburnt hydrocarbons in car exhaust gases. The simplest mechanism of formation of ozone in a clean environment is the oxidation of carbon monoxide in the presence of nitric oxide. The destruction of ozone is also catalysed by nitrogen oxides.

Ozone does not have a direct effect on stone but it can be important in that it is a strong oxidising agent. In certain instances, e.g. sulphate formation in cloud water, uncatalysed oxidation of $SO_2$ by ozone may dominate the relatively slow reaction between $SO_2$ and oxygen.

Aerosol Particles
The troposphere is the closest region of the atmosphere extending between 8 Km and 17 Km from the earth's surface. It contains about 70% by weight of the total atmospheric gases and 99% of the total aerosol. These particles are important for [37]:

- Cloud and precipitation formation.
- Atmospheric radiation balance.
- Their ability to influence chemical conversion processes, e.g. $SO_2$ oxidation.

Approximately 20% of the total aerosol is thought to be of man-made origin while the remaining 80% is from natural sources such as sea salt, wind-blown dust, volcanic emission and forest fires. Concentrations of suspended particulate matter in the atmosphere have been found to follow yearly, weekly and daily cycles. In urban areas of the United States concentrations were found to be higher during week days [18]. The daily cycle in urban areas shows two maxima, one at 8 - 9 a.m. and the other at about 6 p.m. resulting from several causes including [38]: (i) the fuel consumption cycle, (ii) increased domestic heating in the morning and (iii) the effect of suspended particulates blown from outlying industrial regions. Measurements made in Venice in 1972 and 1973 showed a seasonal trend for concentrations with winter values approximately twice those of summer [4].
Suspended particulate matter can have a detrimental effect on stone by dirtying surfaces, causing both aesthetic damage and at the same time creating conditions for oxidation processes catalysed by metal particles present in the dirt. Removal of particles from the air is by both wet and dry deposition to the earth. Particles of size 0.1 - 1 \( \mu \text{m} \) are mainly removed by incorporation as condensation nuclei during cloud formation. Large particles are mainly removed by dry deposition due to sedimentation.

### 1.2.2.2 The Formation of Black Crusts on Stone

The formation of unsightly and potentially damaging black crusts on stone buildings and monuments is an all too familiar problem, particularly in industrial and urban areas. However, this is not a new phenomenon; smoke damage to temples resulting from wood burning was recorded by poets in ancient Rome [39]. In south east England the shift from wood to coal as a fuel began in the 13th century when wood supplies began to run out around some major towns. The switch to coal brought about dramatic changes in urban air pollution with the increase in \( \text{SO}_2 \) concentration being especially damaging to stone. By the late 16th century the domestic use of coal had become widespread in England and in particular London. The success of coal as a fuel led to a rapid increase in the density of its use in urban areas and by the mid 18th century smoke concentrations had risen dramatically; in London more than one million tons of coal were used each year in an area which had not grown appreciably since medieval days. It is believed that in about 1900 soot and \( \text{SO}_2 \) concentrations were higher in many cities than they are today. In London the decrease since 1900 is probably due to expansion of the city with the development of an urban transport system.

During the past 30 years many buildings have been cleaned of the black deposits resulting from combustion of fossil fuels, but are now becoming soiled once more. The contribution of coal burning to soiling is decreasing and emissions from diesel engines are now thought to be the major source of soiling matter in urban areas [40]. Diesel exhaust is a source of very fine carbon particles, about 0.02 \( \mu \text{m} \) in diameter, which are chemically inert but very sticky and likely to adhere strongly to a stone surface. Pollutant gases such as \( \text{SO}_2 \) and nitrogen oxides (\( \text{NO}_x \)) are readily absorbed onto the surfaces of such particles which can act as catalysts in the conversion into sulphate and nitrate forms. At present \( \text{NO}_x \) emissions, particularly those from vehicle exhausts, are increasing which partly explains why rates of building erosion are similar to when \( \text{SO}_2 \) and soot concentrations were much higher than they are now. Measurements made on the balustrades at St. Paul's Cathedral [10] indicate that during
the 18th century limestone was being eroded at a mean rate of 8 mm every 100 years and that the rates today are similar despite a substantial decrease in SO$_2$ and smoke levels.

Considering building facades, there tends to be a fairly even accumulation of dirt on vertical surfaces except where some feature causes a concentration of running water which often produces a lighter cleaner streak across the dirt. This effect is known as *white washing*. Dirt will usually accumulate to a greater extent on sills and horizontal or near-horizontal surfaces, and run-off water can carry dirt to adjacent vertical surfaces where it collects to produce dark dirty streaks. This effect is called *dirt washing*. Exposed stone surfaces can, in general, be divided in terms of black, grey and white areas [4,41];

*Black areas* are found on parts of the building sheltered from direct rainfall and surface runs. These hard black crusts have four basic components [42]:

(i) Inorganic airborne particles (soil, dust, smoke).

(ii) Organic airborne particles (plant remains, pollen).

(iii) Inorganic precipitates (perhaps produced in situ, e.g. gypsum on limestone).

(iv) Organic growth in or on the crust (bacteria, fungi).

The black pigmentation of the crust is due to a number of factors including smoke particles which can vary in size between 0.02 $\mu$m and 100 $\mu$m. Smoke particles include all products of combustion ejected into the atmosphere including domestic, commercial and vehicle sources with coal, oil and diesel internal combustion sources.

*White areas* are often found on surfaces of calcareous stone directly exposed to rainfall. Such surfaces are subject to a mechanism which regularly removes deterioration products formed on the stone surface by rain washout. The combined effect of deterioration and regular washout results in a thinning of the stone although the surface morphology is often unaltered. Analyses have shown that the surface of the white areas is mainly composed of recrystallised calcite [41].

*Grey areas* are often observed inside porticos and arcades where beating rain and washing out are prevented, even if condensation is possible [41]. The stone is covered
by a thick, compact layer of dust particles and deterioration products. Thickening and hardening of the layer is slow compared to hard black crusts, possibly as a result of the surface exposure which does not allow the pollutant to remain in contact with the stone long enough to react completely. The morphology of the original stone is maintained as no physical or chemical interaction occurs between the dust particles and stone.

Black crusts formed on calcareous stone have been found to be composed largely of gypsum crystals mixed with black carbonaceous particles produced by fuel combustion which are active as catalysts in the transformation of calcium carbonate into calcium sulphate. Major elements present in these spherical, black particles are silicon, sulphur, aluminium and calcium with small amounts of potassium, vanadium, iron and copper [43]. The main sulphur compounds found in these particles are sulphates, sulphites and SO$_2$ which are adsorbed on the surface. Analysis of black crusts removed from statues and monuments in Venice showed the main component to be sulphate (20 - 30%) [29]. On detailed stonework, especially sculptures and balustrades, crusts can be very thick and sharply defined. In these cases the crusts are built up by dry deposition and can be several millimetres thick. Figure 1.6 shows a limestone sculpture of a grotesque which has been removed from the exterior of Lincoln Cathedral. Hard black crusts up to 15 mm thick have formed in areas sheltered from direct rainfall. Lincoln Cathedral (see figure 1.7), mainly constructed between 1072 and 1280, is situated on a hill in the low-lying east of England, exposed to the prevailing south westerly winds. Although the city is in a rural setting the cathedral overlooks the coal-fired power stations of the Trent Valley, about 20 Km away. Since 1950 emissions from power stations and vehicle exhausts have played an important role in Lincoln air pollution and hence in the degradation of stonework at the cathedral [44].

Although black crusts are often thick, hard and compact they do not form a protective layer. Crusts are seldom continuous and impervious to water due to the presence of cracks. The high solubility of calcium sulphate with respect to calcium carbonate causes long gypsum crystals within the crust to allow penetration of water inside the stone. Often beneath the crust, stone appears to undergo recrystallisation up to a depth of several millimetres, forming an alteration layer composed of a mixture of gypsum and calcite crystals with embedded carbonaceous particles [43]. Black crusts are also frequently associated with weathering processes, especially salt crystallisation, which cause volume expansion behind the crust (blistering), disaggregation of the stone.
matrix and eventually cause crust and substrate detachment. Material loss can be severe and newly exposed stone is more susceptible to further weathering. Examination of crusts which appear to have left the stone unaffected often reveals decay processes having already occurred causing irreversible damage.

On other types of stone which do not have a significant calcite content, air pollution tends to form a thin, hard black layer at the surface [45]. Such layers, usually 0.02 - 0.2 mm thick, are often seen on quartz-cemented sandstone, granite and sometimes brick surfaces. The composition of these layers is complex and not fully understood, but
research has shown that iron and sulphur concentrations are generally higher at the surface than inside the undamaged stone. The black colour is caused by dark coloured iron compounds or soot, or both. The increased iron concentration at the surface is thought to originate from the stone itself, as well as from air pollution. In country areas with no industry and little traffic, surface iron can result from reactions between acid rain and iron-containing minerals in the stone, such as pyrite, limonite and micas. The increased sulphur concentration results mainly from air pollution. Surface carbon, which is usually bound in the form of soot (graphite) and organic compounds, is due to emissions from traffic, industry and power plants. Thin black layers on non-calcite building stone may be composed of more than 100 different compounds. The accumulation of such a layer is not only aesthetically damaging but can also cause exfoliation of the stone surface.

Hard dark crusts common on the surface of weathered sandstones in Glasgow are composed of airborne pollutants such as soot, algae and lichen and minerals drawn from the interior of the stone which have been reprecipitated on the surface. Glasgow sandstones are generally quite porous allowing water to penetrate into the stone and...
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later egress and evaporate at the surface. During this cycle fluids are able to dissolve unstable minerals from within the stone and reprecipitate them on the surface, forming a tough, outer layer known as *patina* and leaving a zone of softer stone beneath from which certain minerals have been removed [46]. As the patina develops it incorporates soiling from sources such as industrial pollution and algae. Dirt adheres to the surface during wetting of the stone and is incorporated as the surface dries out. The crust may eventually become so thick and impervious to water that moisture is unable to leave the stone. Moisture then builds up behind the crust where it can react to break down the stone. A heavily weathered sandstone may develop up to five different zones in the stone [47], as shown in figure 1.8;

![Diagram of heavily weathered sandstone]

**Figure 1.8: Diagrammatic representation of a heavily weathered sandstone [47].**

1. **Outer zone;** approximately 1 mm thick, composed of pollutants such as soot, and also algae and lichen.

2. **Zone where pollutants are mixed with minerals brought from within the stone and reprecipitated on the surface.** This is usually a tough, dark zone between 0.5 and 5 mm thick.

3. **A discoloured zone due to heavy mineral reprecipitation.** This part of the patina is 5 - 25 mm thick and is well cemented by minerals leached from within the zone.

4. **A friable zone which has been depleted of minerals in the formation of a patina (zones 2 and 3).** It is the weakest zone in the outer boundary of the stone.
5. Original or close to original stone as quarried.

1.3 The Cleaning of Stone Monuments and Buildings

The cleaning of stone buildings, monuments and sculpture is necessary for both aesthetic reasons and to ensure better preservation of the materials involved. Thick black crusts can completely transform the appearance of sculpture by effectively turning it black, altering its texture, obscuring fine detail in the carving and in worst cases rendering the outline of the stone invisible. As discussed in the previous section black crusts can lead to deterioration of the stonework as well as hiding the effects of other weathering processes. Careful and skilled cleaning of sculpture can often successfully restore its outer appearance and reveal weathering effects before irreplaceable loss of original material occurs.

1.3.1 Adhesion of Dirt to Stone Surfaces

Particles of dirt are often bound very strongly to the stone surface, making their removal without causing irreversible damage to the substrate a very difficult and, sometimes, impossible process. The adhesion of solid, liquid and gaseous particles to a solid substrate depends on secondary bonds [4]. Secondary bonds, as opposed to primary bonds (ionic, covalent and metallic) which produce strong forces holding atoms together to form molecules or crystals, produce forces which hold molecules together. In dry surroundings the main forces of adhesion on stone surfaces are: (i) electrostatic, (ii) secondary Van der Waals forces and (iii) hydrogen bonding;

*Electrostatic action* is generated by electric charges which form in the contact interface between two materials. Aerosols may already be charged before they come into contact with the stone surface, e.g. by ionising radiation in the atmosphere, or they may become charged at the moment they are deposited onto the stone.

*Van der Waals* forces are generated by dipole interaction between two molecules. A dipole can be induced on a molecule by the permanent or instantaneous dipole moment of another molecule, thereby creating a force of attraction between the two. Therefore, there exists a weak attractive force acting between all atoms and molecules at all times, allowing molecules to stick together even when there are no attractive forces due to permanent charge separation in the molecules themselves [48].
A **hydrogen bond** is formed by electrostatic attraction between a hydrogen atom bonded to an electronegative atom and another electrically negative atom.

In general, dirt adheres to a stone surface by one or other of these secondary bonds. The main force of adhesion of small particles, less than 50 μm diameter, on a dry surface are Van der Waals forces [49]. Electrostatic forces become important and predominate for particles larger than 50 μm diameter. Electrostatic forces also play an important role in bringing particles to the surface of the stone for adhesion. The total adhesive forces acting on a particle of only 1 μm diameter can exceed gravitational forces acting on that particle by a factor greater than $10^6$. In a humid atmosphere other forces due to capillarity and surface tension will be active. The problems of cleaning can be considered as comparisons of the strength of adhesion between the dirt and object being cleaned and the cohesion of the molecules of the object to one another. Dirt which is weakly bound to a strong object should be easy to remove without damaging the object (unless dirt is trapped in pores and cracks in the object), whereas dirt which is strongly bound to a crumbling object presents difficult problems.

### 1.3.2 General Criteria for the Cleaning of Stone

The choice of cleaning techniques must be considered very carefully to avoid causing irreversible damage to the stone surface. Loss of original stone can result from the employment of an unsuitable technique, as well as from lack of skill and experience on the part of the operator. Since it is desirable to preserve the original aspect of a building, monument or statue to the greatest possible extent, large losses of material from the surfaces are not acceptable. Cleaning techniques must, therefore, be carefully selected according to the following criteria [50]:

- They must not harm, directly or indirectly, the stone being cleaned.
- They must allow the most extensive preservation of the patina possible.
- They must not produce by-products which, remaining in these stones, may affect the future preservation, e.g. soluble salts.
- Cleaning speeds must be controllable so that the operator can adjust and stop cleaning instantaneously.
They must result in a clean and smooth surface, as free from cracks and holes as possible.

Cleaning methods must be determined for each individual case. It may be necessary to use several different cleaning methods on one building depending on the various states of decay and types of dirt present in different areas. Less restrictive criteria may be more suitable for buildings of little cultural interest. Other factors which should be taken into consideration are:

- The chemical and mineralogical structure of the stone.
- Porosity of the stone.
- Previous treatments to the stone.
- The cost, time required and the availability of skilled workers for the various specialised operations.

When sculpture of historical and cultural interest is to be cleaned, the cost factor should be of secondary importance only. Any proposal to clean must be preceded by a detailed survey which can be carried out at three different levels [51]. In the case of a building facade this may take the form of:

(i) A relatively superficial inspection from existing vantage points to identify the general type and condition of the fabric and extent of soiling. It should also look at the condition of adjacent buildings. Such a survey should establish the desirability of cleaning and help to form an idea of how the cleaned building would look.

(ii) A preliminary survey, designed to establish the most appropriate methods of cleaning and to assess accurately the extent of stone repair which will be involved and how the building will appear after cleaning. Possible disruptions to the occupants and public should be discussed and evaluated.

(iii) A detailed survey involving trial cleaning should be carried out to establish the final specification and to ensure as many future problems as possible are anticipated. Trial cleaning should not be carried out on the most prominent part of a building but should include as many typical problems as possible. Such
areas are usually found on openings, open joints, under overhangs and in the vicinity of old repairs and staining.

Cleaning methods can be divided into groups according to the technique used:

(i) Water-based methods: water sprinkling, water spray with or without pressure, steam, very fine water spray (mist).

(ii) Mechanical methods: wet-abrasive, dry-abrasive, micro-abrasive.

(iii) Chemical methods: acid and alkaline solutions.

(iv) Poulticing.

(v) Laser cleaning.

The first four groups of cleaning methods will be described in the following section.

1.3.3 Cleaning Methods

1.3.3.1 Water-Based Cleaning

Water is commonly used in cleaning stone as it has a number of advantages: it is cheap, readily available, non-hazardous to the conservator and the strong polarity of its molecules means that it is able to dissolve salts which most organic solvents do not touch.

Water Sprinkling
This technique involves sprinkling water onto the surface being cleaned until the deposits of dirt are softened. This is followed by vigorous scrubbing and rinsing to remove the dissolved crust. The patina and crust of the stone are usually left fairly intact, but complete removal of dirt is often a problem. This technique is time consuming and requires large quantities of water which can result in serious secondary effects, such as water infiltration and freezing damage. Water penetration can lead to movement of soluble salts through the stone which may cause damage upon crystallisation. In severe cases soluble salts may be transported onto internal surfaces
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during evaporation processes where they could cause damage to mural paintings, for example.

Water Spray
A jet of water is fired under high pressure onto the soiled surface for a period which is sufficient to produce swelling of the dirt layer. Soluble material is washed away with the water, and the remaining crust is removed by scrubbing with a nylon or bristle brush. The amount of water used should be kept to a minimum and cleaning should not be carried out in winter because of the risk of freezing damage due to insufficient evaporation. The flow of water should be directed from the top and downwards so that lower areas of dirt are softened by the running water.

This technique has been successful in the removal of soluble salts on limestones, but is less effective on heavily encrusted areas. Water spray has been used extensively in Britain where the high pressure lance method was applied to certain monuments for periods varying between 3 hours and several days depending on the degree of soiling. Monuments where this technique has been employed include: Lincoln Cathedral; Exeter Cathedral; St. John's College, Oxford; Westminster Abbey, London [52].

The water spray technique should not be used on badly decayed stone since it can lead to a crumbling of superficial layers of the stone. The release of small flakes of stone can result from the dissolution of salts. Such flakes may be attached by soluble salts present as the result of activity between a polluted atmosphere and the stone surface. Staining and the appearance of white efflorescences can occur due to salt migration to the surface. Water penetration, especially through defective mortar joints can be a problem and the mechanical action of brushing away stubborn deposits from a stone surface can lead to damage of the crust.

In cases where the stone is weak it is advisable to use nebulizers, which are highly efficient although they require little water. Special nozzles deliver water to the stone surface as a fine mist made up of very small droplets with a large specific surface. Nebulized water is deposited on the stone practically under no external pressure and is very efficient in dissolving black crusts. At the Palace of Westminster [53] the stone was exposed to a fine mist of water from a series of nebulae nozzles attached to a length of pipe connected to the mains. Limitations were imposed on the quantity of water passed through each nozzle and the period of washing was restricted to one hour on, two hours off in an attempt to avoid saturation and water penetration.
Steam Cleaning
Steam generated by a boiler is directed under pressure at the stone surface by a lance. As with the previous methods brushing away remaining dirt may follow washing. The steam pressure can be controlled by the operator. Steam cleaning causes minimal wetting and the pressure of the steam can mechanically remove dirt from details which might otherwise prove difficult to clean [51]. To clean effectively, the nozzle should be held near the surface to blow layers of dirt from the stone. One advantage of steam over water is that the surface dries out rapidly after cleaning, thereby allowing other processes such as consolidation to be carried out almost immediately.

Steam cleaning should not be used on friable surfaces and extra care must be taken to remove dirt without damaging the surface where fragments of paint remain or surfaces are damaged in some way. Before starting, cleaning tests should be performed on the stone to ensure that it can resist the relatively high temperature of steam. If the stone is porous and retains large quantities of vapour efflorescence and humidity stains can occur. The technique can be used on a large scale, for the external cleaning of buildings, or on a small scale for the cleaning of sculpture.

1.3.3.2 Mechanical Cleaning
Mechanical cleaning techniques involve arranging a collision between the dirt and some material object. The aim of the collision is to produce a force which will: (i) break the contact between the dirt and stone surface and (ii) remove the dirt from the object [48]. To clean the stone without damaging the surface requires the break to occur at the interface between stone and dirt, whilst ensuring that the method used to produce the break actually strikes the dirt and not the stone. Mechanical cleaning methods have some advantages over water-based methods since nothing is added to the stone which might encourage further deterioration such as water causing swelling in hygroscopic materials. However, almost all mechanical cleaning methods require eye, skin and lung protection for the operator. Before such a method is chosen, several questions should be answered:

(i) How firm is the adhesion between dirt and stone?
(ii) Is the dirt brittle or tough?
(iii) What are the mechanical properties of the stone?
Often, dirt layers are bound very strongly to a weak stone surface. Complete removal of all the dirt would, therefore, result in damage to the weakened surface, especially if dirt has penetrated into the pore space. To avoid overcleaning, shown in figure 1.9, it is often necessary to leave some of the dirt on the surface. The degree to which such a surface can be cleaned without damage depends to a large extent on the skill and experience of the operator.

![Figure 1.9: Different levels of cleaning showing how damage can occur through overcleaning.](image)

**Picking Methods**

Splitting off black crusts with scalpels, needles and dental picks and pinging or picking off small flakes is a method which is sometimes used on porous layers [48]. It is most often used to break up a hard, brittle crust piece by piece and remove it from the surface of the stone. In order to successfully remove a crust without damaging the underlying stone the blade or needle has to fracture the crust through its thickness, then the fracture plane must turn suddenly and proceed along the interface between dirt and stone, as shown in figure 1.10. This form of mechanical cleaning exploits the difference in physical properties between the dirt layer and stone. As the blade moves deeper into the dirt a sideways force is applied which may be sufficient to overcome the adhesive forces between dirt and stone and break off a small chip, as shown in figure 1.11. The picking method only works with brittle dirt of reasonable thickness on a stone surface in good condition. If a layer is brittle the crack will run on ahead of the blade down to the interface with the stone. If, however, the dirt is too tough, the blade will reach the stone before the crack runs on, causing damage to the stone.
Figure 1.10: Intended path of fracture in a dirt layer to be removed by picking.

Figure 1.11: Removal of a section of crust by picking.

**Abrasive Cleaning Methods**

Abrasive methods work by cutting away deposits of dirt, as opposed to picking methods which snap off the unwanted material. The cutting edges are usually hard, sharp particles carried in a blast of air. On impact with dirt, or stone, the sharp edges hack away small fragments from the surface. Several factors must be considered carefully when cleaning by abrasive methods:

(i) The relative hardness of dirt, stone and abrasive; in order to clean a surface the abrasive must be harder than the layers of dirt to be removed. However, black crusts are often harder than the underlying, and sometimes crumbling, stone. In
this case removal of the crust is followed by damage to the surface of the stone, the degree of which depends on the state of the stone and the skill and experience of the conservator. Problems may also be encountered when the crust and stone are not uniformly hard. Examples of abrasive powders are aluminium oxide and carborundum.

(ii) The size of abrasive particles; the same abrasive is often available in different sizes; coarser particles are used for preliminary cutting work on thick crusts, while finer particles are used for finishing and more careful work, such as cleaning decayed stone.

(iii) The force with which abrasive particles strike the surface; particles carried on a stream of compressed air under high pressure are travelling faster and, therefore, have more impact on the target surface than particles under low pressure.

(iv) The use of water in conjunction with the abrasive; water can act as a lubricant, lessening the effect of the abrasive particles, and reduces dust.

*Wet grit blasting* consists of blowing a mixture of water and abrasive at a pressure varying between 5 and 30 Ncm⁻² [4]. The basic equipment consists of an air compressor, a pot for the abrasive and air and abrasive delivery lines. In some types of system water is carried along a separate hose to the end of the abrasive delivery line where it is discharged as small jets into the air and abrasive streams. Several factors can be controlled and should be monitored closely: abrasive/water ratio, abrasive size and hardness, compressed air pressure and distance between the lance and stone. This technique does not produce dust but must be followed by a final rinsing operation with water. Wet blasting is appropriate for use on heavy crusts of dirt but should be avoided on monuments of historical and artistic interest since the large amounts of water used mobilise soluble salts inside the wall and give rise to crystallisation during evaporation.

*Dry grit blasting* projects only abrasive through a nozzle in a stream of compressed air. This technique is difficult to control and often results in extensive loss of patina and in partial loss of the original relief of damaged carved stone. Blasting with abrasive and no water requires thorough safety precautions due to the health hazards caused by large quantities of harmful dust; the operator must be protected by a helmet supplied with filtered air and should wear full protective clothing. Precautions must also be taken to ensure dust does not penetrate into areas, e.g. the interior of a building, where
it can cause damage. Cleaning by dry blasting avoids water penetration and subsequent staining or efflorescence. On simple facades the technique is probably the fastest way to clean safely. Another advantage over wet blasting is that the operator can immediately see the result of the cleaning.

*Micro-blasting* is essentially a refined version of dry grit blasting which is suitable for cleaning on a small scale, particularly where water could be disruptive. Microscopic abrasive particles (particles of aluminium oxide, 27 µm in diameter, are often used) are ejected in a stream of compressed air from a nozzle about 1 mm diameter at the tip of a small pen-like gun. An extractor should be placed close to the nozzle since micro-blasting produces considerable amounts of dust. All parts of the machine exposed to the abrasive are subjected to abrasion, in particular the nozzle, and need replacement from time to time. In skilled hands this technique can be used on:

- Thick and hard crusts.
- Thin crusts.
- Badly damaged stones.
- Deposits of dirt covering paint, which would be removed by other techniques.

In many cases where thick black crusts cover the surface of a sculpture, micro-blasting is the only technique available to the conservator which will remove the crust without wetting the surface [51]. On small scale fragile detail, especially where salt crystallisation damage has occurred, micro-blasting (if used skilfully) is safer than water cleaning. However, although cleaning can be carefully controlled, by the very nature of the technique damage of the stone to some extent (usually as loss of surface material) is unavoidable.

**Vibrations**

Another mechanical method of dislodging particles of dirt is to use a vibrating tool to break up the unwanted crust. In some commercially available tools electrical pulses are used to produce vibrations in points (such as a needle) of different sizes for cleaning and engraving. These tools are basically automatic versions of the hand-held needle, used for picking. Care must be taken to avoid vibrating the object so much that damage is caused and to stop at cleaning and not start engraving [48].
The cavitron is a cleaning system which has been adapted for conservation use from an ultrasonic, dental de-scaling tool [51]. A delicate ultrasonic vibration is produced in the tip of a pen-like tool, under which a jet of water is passed. The passage of water under the tip forms a gentle bubbling action which is able to remove particles of dirt when the tip is placed close to the surface of the stone. This technique is very efficient in removing dirt particles trapped in undercuts and crevices. However, if the vibrating tip comes into contact with the stone then a small pit will be formed.

1.3.3.3 Chemical Methods

In some cases chemicals are used to clean stone. This method requires expert supervision otherwise chemical products may cause irreversible damage.

Certain acids and acid salts clean by reacting with black crusts and dissolving them. Acid is applied to the surface in a number of ways: (i) by brush, (ii) using low pressure spray and (iii) as a gel. The area to be cleaned is often wetted prior to acid treatment to provide a damp surface on which the chemical will spread. After the correct time the acid is thoroughly washed off, often using a low volume water lance. Acid cleaning is quiet and avoids many of the risks associated with unskilled abrasive cleaning. However, acids are potentially dangerous to both the operator and the stone. Cleaning with acids often appears promising in the short-term but may eventually lead to accelerated weathering. Effects which have been observed include [46]:

- **Staining and bleaching;** these result from chemical reactions within the stone in which unnatural amounts of a substance (e.g. iron) are released to the surface, leaving a depleted region behind.

- **Efflorescence and salt disturbance;** this is a direct result of the application of chemicals which react to produce salts. These salts are formed in two ways: (i) by dissolving minerals within the stone and reprecipitating them on, or close to, the surface and (ii) by the reaction between two applied chemicals forming new salts on the surface - in some cases an acid and alkali are used together so that one will neutralise the other within the pores of the stone.

- **Algal growth;** strong acids can leave constituent mineral surfaces etched and pitted, effectively increasing the porosity of the stone. This can lead to increased water retention which encourages the growth of algae.
Other disadvantages of using acids and chemicals in general are the inability to control their movement within a stone and the inability to monitor their reaction [47]. The operator is unable to assess how far solutions have penetrated into a stone and to halt aggressive reactions, or to prevent the solutions from migrating to areas which are susceptible to damage. The operator is also often unable to make an instant visual assessment of the reaction at the interface between stone and dirt until the reagent has been washed off, by which time the stone may already have been irreversibly damaged.

Two acids which have been previously used in cleaning stone are hydrofluoric and hydrochloric acid. Hydrofluoric acid has been used to clean sandstone buildings in Glasgow, where the above effects have been observed. Studies carried out in Glasgow [46,47] concluded that chemically cleaned buildings within the city are efflorescing, staining, decaying and soiling at a faster rate than those cleaned by mechanical methods.

Alkalis are able to destroy cohesion in grease stains and have been used successfully in the removal of black crusts from limestone and marble [4].

On a small scale the cleaning of stone surfaces using solvents and reagents applied by a small cotton wool swab has been successful [51]. Mixtures of acetone or white spirit with water are effective in cleaning thin deposits on limestone surfaces. On marble methylene chloride, white spirit and acetone can all be used. In the hands of a skilled and experienced conservator these chemicals can be used safely, but if applied carelessly and not properly neutralised the stone can be badly damaged.

1.3.3.4 Poulticing

To avoid deep penetration and to limit the action of chemicals on the stone, they are sometimes mixed with absorbent powders to form a paste or poultice. The technique of using a poultice to draw out dirt from stone developed from a process which used poulacies of paper pulp to remove salts from stone [54]. By applying a water poultice to the stone a layer of water is suspended over the surface and kept there as the dirt is dissolved [51]. As the poultice dries the water evaporates and slowly draws the dirt back into the poultice. After several hours the mud begins to fall away from the surface of the stone. The remainder of the poultice is then removed and the stone cleaned with swabs and small quantities of de-ionised water. Water poultices are mainly used for cleaning marble, limestone and some sandstones. One of the most commonly used
poultices is made up of de-ionised water and sepiolite (magnesium silicate). Using a poultice to clean stone has the advantage of wetting only the surface; penetration of water into the stone is minimised and disruption of salts and minerals is, therefore, avoided. Careful use of this technique will even allow removal of dirt from painted stone without damage.

1.3.3.5 Summary

Traditional methods of cleaning stone can be divided into four categories: (i) water-based, (ii) mechanical, (iii) chemical and (iv) poultice. In the hands of a skilled and experienced conservator who understands the nature of the materials involved and the principles being used, these techniques can often be successful in removing layers of dirt and restoring the outer appearance of stonework. However, if used carelessly they can do more harm than good. Loss of material, staining and mineral depletion are types of damage caused to stonework which may not only contribute to disfigurement but also to accelerated weathering, thereby shortening the life of the object. Since each of these methods involves some kind of contact with the object, either mechanical or chemical, it is not possible to clean an object without causing damage, which may or may not be visible. It is not possible to remove layers of dirt from stone by mechanical methods without causing collisions between abrasive particles and the stone surface. Any solvent or reactant applied to stone and its dirt causes chemical collisions with both and although the dirt may be removed, traces of the chemical used will always remain. Provided cleaning is successful in restoring the aesthetic qualities of the building or sculpture, and slows or halts its deterioration then it should be carried out. It is important to remember that whatever method of cleaning is used, damage to some degree will occur. It is the job of the conservator to minimise the damage caused, whilst restoring the appearance of the object as near as possible to that intended by the sculptor.

1.3.4 The Use of Lasers in Cleaning Stone Sculpture - Previous Work

In 1972 a group of researchers from the University of California undertook a feasibility study in Venice to determine whether holography could be used in the conservation of stone sculpture [55]. During the first three months of that year a pulsed ruby laser was used in situ to make archival holograms of crumbling sculpture. These holograms demonstrated the feasibility of this means of 'preserving' works of art in three
dimensions. During this work the collaboration of laser scientists and conservation scientists led to the discovery that a pulsed ruby laser is able to selectively remove layers of dirt from decaying marble sculpture. The idea of selectively vaporising an optically absorbing substance from a reflective surface was not new; soon after the invention of the laser in the 1960s Arthur Schawlow proposed a tool called the 'laser eraser' which was able to selectively vaporise black pigment from white paper. Black pigment absorbs a large proportion of the incident laser radiation which may be sufficient to cause vaporisation. White paper, however, is strongly reflecting so once the pigment has been removed further pulses of radiation are harmlessly reflected away and vaporisation stops. Asmus suggested that this simple principle also applies to the removal of layers of black dirt from a white stone surface [56-59].

It was suggested that the effect a pulsed laser causes on the surface of a sculpture is dependent on the colour, boiling point and/or dissociation temperature of the material being irradiated. When a beam of light is incident on a surface the temperature rise at the centre of the illuminated spot is given by [60]:

\[ T(t) = \frac{2\alpha I}{K} \sqrt{\frac{kt}{\pi}} \]

where 
- \( t \) is time
- \( \alpha \) is surface optical absorptivity
- \( I \) is incident laser beam power density (Wm\(^{-2}\))
- \( K \) is material thermal conductivity
- \( k \) is material thermal diffusivity

For a spot size of a few millimetres an output of 10 KW from a pulsed laser may be sufficient to induce a maximum temperature rise given by [6]:

\[ T = (1.7 \times 10^3)\alpha \, ^\circ C \]

Thus, for a black, strongly absorbing (\( \alpha \approx 0.9 \)) crust on stone the temperature rise might be as much as 1500 °C. For a white, strongly reflecting surface (such as the underlying stone, \( \alpha \approx 0.1 \)), the temperature rise might be only 170 °C. Asmus suggested that, assuming \( \frac{\sqrt{K}}{K} \) for the crust and stone are equal, selective removal of the crust is possible provided the following relation holds:
where $T_B$ and $T_B'$ are the boiling points of the stone and encrustation respectively and $\alpha$ and $\alpha'$ are the corresponding surface absorptivities.

If the ratio of stone and encrustation boiling points is plotted against the ratio of the optical absorption coefficients, an area of the graph can be seen where selective divestment is possible, as shown in figure 1.12.

![Figure 1.12: Conditions for selective removal of dirt layers from stone.](image)

The area shaded \( \text{\textbackslash textbackslash textbackslash textbackslash} \) is favourable for boiling point discrimination. The area shaded \( \text{/ / / /} \) is favourable for absorption coefficient discrimination. Where the two areas overlap both mechanisms contribute to the selective cleaning action.

To test the validity of this model a pulsed ruby laser beam was focused onto the polluted surfaces of friable Italian marble fragments which were then examined by scanning electron microscopy and x-ray fluorescence. To begin with a very low laser fluence (energy contained in a single laser pulse divided by the area of the pulse) was used. The fluence was increased in small steps until an effect was observed. The selective cleaning characterised by the planar heating model in figure 1.12 was evident. One or two pulses at the vaporisation threshold were usually sufficient to remove a black crust 0.2 mm thick with further pulses having no observable effect on the underlying marble.
A pulsed ruby laser can be operated in two different modes: (i) Q-switched and (ii) fixed-Q. Operating fixed-Q the laser emits pulses of the order of $10^{-3}$ s duration. Operating Q-switched the pulse duration is considerably reduced to about $10^{-8}$ s. Between 1973 and 1975 experiments were carried out at the University of California to improve the understanding of the cleaning process. Asmus concluded that there are two main interaction mechanisms by which laser cleaning is achieved:

(i) Fixed-Q radiation cleans by selective vaporisation as shown in figure 1.13:

![Initial and final interaction of fixed-Q laser radiation with a black crust.](image)

(ii) Q-switched radiation cleans by spallation. With pulses of such short duration flux levels can be attained at which even relatively reflecting surfaces absorb sufficient energy to cause vaporisation. The vaporising material itself then absorbs additional energy from the incoming laser beam and can reach temperatures of $10^4 - 10^5$ °K. At this temperature the vapour is ionised and absorbs the laser energy very strongly so the solid surface is shielded from the laser beam. The initial surface evaporation, therefore, comes to a halt. However, as the laser pulse continues, the plasma (ionised gas) is heated and can reach a pressure of 1-100 Kbar. The plasma pressure produces a microscopic compression of the surface material. At the end of the laser pulse, the plasma expands away from the surface, the surface material relaxes and spallation removes a thin surface layer, as shown in figure 1.14.
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Figure 1.14: Effect of Q-switched radiation on a material surface.

According to Asmus, both of these cleaning mechanisms have advantages. Q-switched radiation is more efficient in removing material and the laser pulse is of such short duration that thermal energy can only be conducted into the underlying material through plasma reradiation. Thus, thermally-induced microcracking is improbable. Fixed-Q radiation, however, appears to be more selective in that it will not remove light-coloured marble whereas repeated Q-switched pulses may lead to damage. Conservators who studied the interactions of Q-switched and fixed-Q radiation with polluted sculpture were of the opinion that the most friable stones showed fewer signs of damage when subjected to fixed-Q cleaning.

The principle practical projects involving laser radiation have been concerned with the marble sculpture of Venice. A neodymium YAG laser (Nd:YAG) has been used in the conservation of a 'Last Supper' sarcophagus lid from Santa Caterina church and the 'Ruskin' capitals of the Palazzo Ducale. In both cases cleaning was successful although problems were encountered; great care had to be taken in overlapping individual laser impact spots to obtain a uniform finish and progress was relatively slow as the laser technology being used was often out-dated.

In addition to the removal of black crusts from marble and limestone, laser radiation has also been successfully used in [58]: the removal of calcareous deposits on pottery, lichens on stone, minerals and corrosion on bronze, overpaints from monochromatic upholstery, encrustations from stained glass [61] and varnish from paintings [62,63]. In 1975 pulsed laser radiation was used to remove relatively modern Visari frescos from a wall in the Sala del Consiglio, Florence, to reveal a 16th century mural painted by Leonardo da Vinci which had not been seen since 1565 when the room was renovated [64].
Asmus concluded that laser cleaning techniques possess a number of unique attributes and advantages over more conventional techniques:

- Selectivity; the laser can effectively be tuned to interact with specific substances through adjustments to the wavelength, pulse length and energy of the radiation. There exist a wide selection of lasers which emit at different wavelengths ranging from the ultraviolet to the infrared.

- Environmentally acceptable; there is reduced dependence on hazardous chemicals and solvents.

- Versatility; optical flux intensities are achievable which can remove many materials.

- Localised action; the laser cleans only where directed.

- Controlled removal; a specific thickness of material can be removed.

- Non-contact; the process involves no mechanical contact with the sample.

However, at the time that this research was carried out lasers were very expensive, the technology largely undeveloped and the cleaning process relatively slow. It was felt that the laser was ideally suited for work on small, badly damaged sculpture. For larger surfaces conventional techniques such as abrasive cleaning provided a more practical and affordable solution. Since then, with the advancements in laser technology and the need for the development of a non-contact, self-limiting cleaning technique it has become necessary to look once more at the feasibility of the laser as a cleaning tool. Since 1987 research has been carried out at the Laboratoire de Recherche des Monuments Historiques in Paris on the interaction of laser radiation with polluted surfaces [65]. A Q-switched Nd:YAG laser has been developed to remove black crusts on a relatively large scale from marble and limestone whilst leaving the underlying gypsum layer intact [66]. Research has shown that the laser is much more selective than abrasive techniques which are often unable to remove layers of dirt without damaging the gypsum layer. Cleaning is now achieved at a rate comparable with more conventional techniques.
Chapter 1: Decay and Conservation of Stone

References


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CHAPTER 2

A COMPARATIVE STUDY OF LASER CLEANING

2.1 Introduction

The interactions of different types of laser radiation and xenon flashlamp radiation with polluted stone surfaces have been studied on a qualitative basis. Four different pulsed lasers have been investigated with outputs extending from the ultraviolet (248 nm) to the far infrared (10.6 μm) region of the electromagnetic spectrum. Most of the work has been concerned with samples of limestone from Lincoln Cathedral. Experiments have also been carried out on marble, sandstone and aluminium samples. Xenon flashlamp radiation provides a diffuse broadband source of electromagnetic radiation with a large ultraviolet component. Such a source was constructed and investigated as a cheap and efficient alternative to the laser for cleaning relatively large flat stone surfaces.

2.2 Flashlamp Radiation

Since the onset of experiments concerned with the laser cleaning of stone it has seemed unlikely that lasers would provide a practical method of cleaning entire stone buildings [1]. Asmus proposed that high energy xenon flashlamps may be useful and efficient in such cases. A xenon flashlamp system is capable of emitting an intense pulse of light of short duration which, when directed at a solid surface, is absorbed by a thin layer of material (typically less than 0.1 mm). In the case of certain materials the energy absorbed may be sufficient to achieve evaporation or chemical breakdown. The flashlamp technique has been used in a number of practical projects, including the divestment of paint from upholstery, layers of overpaint from mural paintings and rust from antique iron [2]. Flashlamp radiation also proved successful in removing encrustations from Venetian marble, but close inspection of the cleaned surface revealed the mineral grains to have suffered slight damage through thermo-mechanical effects [1]. Asmus suggested that flashlamp radiation offers an efficient (xenon flashlamp systems can be an order of magnitude more efficient than a pulsed laser) and cost-effective alternative to the laser if successful divestment does not require spectral purity, action at a distance, or very high energy densities, i.e. flashlamps may be more
suitable on large and relatively flat areas where the substances to be removed are easy to evaporate or break down chemically.

Research carried out in 1984 showed the flashlamp to be effective in removing residual paint from the weathered wooden surface of a totem pole [3]. Although effective the flashlamp was not efficient enough for practical application; half an hour was required to clean an area 15 cm square. It was concluded that flashlamps are useful for the removal of paint and other organic materials from relatively large artefacts, but that development of the equipment and techniques would be necessary before they could be used routinely.

2.2.1 Principles of Operation

The xenon flashlamp is a light source which produces a very high intensity flash from electrical energy stored within a capacitor. During the second world war it was used extensively for aerial night photography and today there are many diverse applications including medical research, lasers and stroboscopes [4]. The spectral output is very similar to daylight in the visible region and there also exist significant ultraviolet and infrared components. The flashlamp essentially consists of xenon gas contained in a quartz envelope, often of linear form, with a tungsten electrode at each end.

In order to obtain a clear idea of how an electrical discharge through a gas generates light it is necessary to understand the mechanism of electrical conduction. In a solid conductor the current is carried by the movement of free electrons through a tightly bound lattice of atoms or ions which, apart from thermal vibrations, are immobile. A metallic conductor has approximately the same number of free electrons as fixed atoms or ions, hence its high electrical conductivity. If an electric current is passed through a conductor the only direct effects are heating of the conductor and the appearance of a magnetic field around it. The emission of light only occurs if the heating is sufficient to excite the atoms and produce incandescence. In a gas, however, there are normally no free electrons and conduction only occurs if the gas atoms are first ionised to produce electrons and positive ions. Under the influence of an electric field electrons freed by the ionisation process can move in much the same way as in a metal, but in addition there is a positive ion movement in the opposite direction to the electron movement. An electric discharge through gas thus consists of two opposite streams of electrons and ions, as shown in figure 2.1.
Figure 2.1: Electric discharge through a tube of ionised gas.

The most important ionising process is ionisation by electron impact. The collision of a free electron with a neutral gas atom can lead to one of three events [5]:

(i) An elastic collision in which the electron rebounds with very little loss of energy.

(ii) The atom may become excited with the electron losing most of its energy.

(iii) The atom may be ionised, releasing one of its electrons.

The probability of any one of these processes occurring depends on the energy of the free electron, ionisation requiring the highest energy. Electron energies are often expressed in electron volts (eV), where one electron volt is the energy gained by an electron accelerated between two points which differ in potential by one volt. The ionisation energy for xenon is 12.1 eV. Thus, an electric discharge in xenon, cannot occur unless at least 12.1 V is applied between the electrodes. However, even when sufficient voltage is available to maintain a discharge through a gas, no ionisation will occur unless a number of free electrons are initially present. Initial ionisation can occur by several mechanisms [5]:

(i) Residual ionisation from a previous discharge.

(ii) Thermionic emission from a hot cathode.

(iii) Photoelectric emission from electrode surfaces.

(iv) Field emission from electrodes.
(v) Ionisation by radioactive materials present in the gas or on the surfaces of the tube.

Each time an electron collides with a neutral atom causing ionisation two free electrons are produced. Successive ionising collisions result in a rapid increase in the number of free electrons and ions as long as losses due to recombination and diffusion to the walls are not excessive. Cumulative ionisation occurs whenever a discharge lamp starts and lasts for a few thousandths of a second. The production of light by a gas discharge is made possible by a process known as excitation in which atoms are able to store energy for a short time. When electron energies are insufficient to cause ionisation, collision with an atom can lead to excitation. Excitation energies are a series of discrete energy levels which correspond to possible orbits of one of the outer electrons of the atom; the highest energy level is equal to the ionisation energy of the atom. An electron in an atom which is raised from the ground state, the lowest energy level, by collision with a free electron remains in the higher level for a short time, typically less than one microsecond. When the electron returns to the ground state the stored energy of the atom is radiated as light. Every energy change has a definite wavelength of light associated with it but not all of the excited states are capable of losing energy by radiation; the lowest excited state that can radiate produces resonance radiation. Resonance radiation is important in a low pressure discharge lamp since it is efficiently generated. In a low pressure mercury lamp resonance radiation is produced in the ultraviolet at 253.7 nm, and can be generated with an efficiency of 50%, i.e. half of the electrical power input is converted into energy covering a very narrow band of the spectrum.

In a high pressure (greater than one atmosphere) gas discharge, e.g. xenon flashlamp, the electrical conduction process involving ionisation by electron collision occurs as in a low pressure discharge but the production of light is modified. Resonance radiation is efficiently re-absorbed by the gas which generates it and very little leaves the tube at high pressure. Other wavelengths of radiation are emitted at high intensity and the mutual interference of closely packed atoms broadens the spectral lines into bands. At very high pressures the radiation emitted by a gas discharge approximates to a continuous spectrum, similar to that produced by an incandescent solid. The high pressure discharge in xenon provides a continuous spectrum which closely resembles daylight with strong components in the infrared and ultraviolet.

Xenon flashlamps are used in pulse conditions and must, therefore, be designed with envelopes, electrodes and seals capable of withstanding heavy loads of short duration.
The lamp envelope is most commonly made from fused-silica based materials. The electrodes are usually tungsten rods. The cathode and sometimes anode have emission coatings which are generally alkaline earth oxides; the cathode must have a sufficiently low work function to allow electrons to be emitted easily, but, at the same time, must not deposit unacceptable amounts of material along the bore of the lamp envelope, limiting lamp life. The trigger connection usually takes the form of a wire around the body of the tube.

A basic circuit for flashlamp operation is shown in figure 2.2. The storage capacitor C is charged to a d.c. voltage V through a resistance R. The voltage V is somewhat less than the spontaneous breakdown voltage of the flashlamp but above the minimum triggering voltage of the lamp. By applying a high voltage pulse to the trigger connection the xenon in the lamp is ionised, lowering the breakdown voltage. This results in a rapid discharge of the capacitor through the gas which produces an intense flash of light [5].

![Figure 2.2: A basic circuit for flashlamp operation.](image)

TrIGGERING of the lamp is normally achieved by applying a high voltage pulse to a wire around the tube. The triggering pulse is obtained by discharging a capacitor into the primary of a pulse transformer [5], as shown in figure 2.3. The main capacitor C₁ is charged from the d.c. source while the smaller capacitor C₂ is charged from a potential divider. When the switch S is closed the energy released from C₂ promotes a high voltage pulse which is applied to the tube and ionises the gas, allowing dissipation of the energy stored in C₁ in the flashlamp.
2.2.2 Experimentation

A linear xenon flashlamp (EGG, type FX47A) was built into the circuit shown in figure 2.4.

The charge resistor $R$ has two functions: (i) to limit the current drawn from the power supply and (ii) to limit the charge current so once $C$ has discharged, the flashlamp can de-ionise and extinguish without 'burn on' which can occur when the voltage on $C$
Reflected radiation

Flashlamp

Target

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exceeds a critical value before de-ionisation takes place. The purpose of the inductor is to reduce the rate of increase of current through the flashlamp as C discharges. The conductivity of a discharge is proportional to the ion concentration which increases with the discharge current [5]. The resultant increase in conductivity is usually so great that the voltage required to maintain the current drops as the current rises. Thus, most discharges are not inherently current limiting. An inductor will introduce a time constant to the circuit to maintain stable operation from a constant voltage supply.

Triggering was achieved by applying a 12 kV pulse from a car ignition coil to a wire around the lamp. The xenon flashlamp was 248 mm in length, with an arc length of 165 mm and an internal diameter of 11 mm.

A flashlamp emits light in all directions. In applications requiring high energy density it is necessary to recover the light emitted backwards, i.e. away from the target, and redirect it towards the target. Ideally, it would be possible to place the lamp and target at the focal points inside a highly reflecting elliptical cavity to maximise the intensity of flashlamp radiation falling on the target. However, it was not practical to build an elliptical cavity. A semi-cylindrical mirror was constructed from highly polished stainless steel and fitted behind the flashlamp as shown in figure 2.5.

![Figure 2.5: A schematic representation (side-view) of the flashlamp and mirror arrangement.](image)

The radius of the mirror \( r \) was determined by sketching the path of the extreme rays emitted by the flashlamp in the direction away from the target. Ray diagrams were constructed for \( r = 2.5, 3.5 \) and 5.0 cm. A radius of 2.5 cm was chosen to minimise the
area over which the radiation was 'focused'. After reflection from the surface of a mirror 2.5 cm radius, rays emitted away from the target were 'focused' into a minimum area of approximately 1.5 x 16.0 cm at a distance of 1.5 cm from the centre of the mirror. At distances greater than 1.5 cm the rays quickly diverged; at 2.0 cm the area doubled.

The flashlamp was tested on black crusts on limestone, soot on brick, paint and varnish on wood, and thermal paper. Each sample was placed between 0.1 cm and 5 cm from the front edge of the mirror and exposed to a minimum of 15 flashes at a rate of 1 flash every 30 seconds. The capacitor was charged to 2 kV.

2.2.3 Results

No cleaning effect was observed on any of the samples; energy absorbed by the surface layers was insufficient to cause evaporation or chemical breakdown.

The maximum incident energy density has been estimated as approximately 0.5 Jcm⁻². The energy E stored in a capacitor is given by:

\[ E = \frac{1}{2}CV^2 \]

With \( C = 40 \mu F \) and \( V = 2 \text{kV} \), \( E = 80 \text{J} \). Assuming the conversion of electrical energy to optical energy is 25\% efficient, each flash contained 20 J. At a distance of 1.5 cm from the centre of the mirror the energy reflected back from the surface (assuming 100\% reflection approximately 10 J) fell over an area 24 cm². Of the energy emitted towards the target only about 3 J fell in this area. Each sample received a maximum of approximately 13 J spread over an area 24 cm².

An energy density of 0.5 Jcm⁻² was insufficient to remove polluted layers. A xenon flashlamp has a broad spectral output and the absorption properties of the sample surfaces are wavelength dependent. Not all of the incident radiation is absorbed by the surface and that which is can give rise to different effects; the ultraviolet component contributes to photochemical effects while the infrared component contributes to photothermal effects. The flashlamp supplied insufficient energy for either of these effects to lead to the removal of material.
2.2.4 Conclusions

Improvements to the design of the flashlamp system could be made:

- By increasing the size of power supply and capacitor and using a flashlamp capable of withstanding higher average powers, the energy emitted in a flash could be increased.

- In order to use the flashlamp at a higher repetition rate a cooling system (circulating water) would have to be added.

- Design and incorporation of a more efficient reflecting and focusing system, such as an elliptical mirror, would concentrate the energy in a smaller area thereby increasing the incident energy density.

It is possible that modifications to the flashlamp system might eventually have led to the development of a system capable of removing weakly bound material, which is relatively easy to evaporate or break down chemically, from a flat surface. However, due to the broadband diffuse nature of the flashlamp output which makes it difficult to focus tightly to obtain high energy densities, it is doubtful whether the flashlamp could provide an efficient method of removing hard, strongly bound pollution layers. It could possibly provide a means of cleaning in cases which do not require high energy density, spectral purity or action at a distance. Due to the broadband output of the flashlamp care would have to be taken to ensure the radiation interacts only with the dirt and not the artefact being cleaned.

Since we are interested in the removal of layers of dirt strongly bound to stone surfaces which are often delicate and intricately carved, the flashlamp was considered unsuitable. It was decided that lasers, which provide a monochromatic output which can be tightly focused to obtain high energy densities, would be more suitable for such applications.

2.3 Laser Radiation

The word LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. In 1917 Albert Einstein demonstrated that the process of stimulated
emission must exist, but it was not until 1960 that T. H. Maiman first achieved laser action, at optical frequencies in ruby [6].

2.3.1 Principles of Operation

When an electron in an atom undergoes transition between two discrete energy levels, it either emits or absorbs a photon. The photon can be described in terms of a wave of frequency \( \nu \) where

\[
\nu = \frac{\Delta E}{h}
\]

where \( \Delta E \) is the energy difference between the two levels and \( h \) is Planck's constant. Consider the hypothetical two level energy system shown in figure 2.6.

![Figure 2.6: Hypothetical energy level system.](image)

By absorbing a photon of energy \((E_2 - E_1)\) an electron in the lower energy level may be excited to the upper level, a process known as spontaneous absorption. An electron which is in the upper level can return to the ground state with the emission of a photon in two ways, as shown in figure 2.7: (i) by spontaneous emission in which the electron drops to the lower level in an entirely random manner, as discussed in section 2.2.1, or (ii) by stimulated emission in which the presence of photons of energy \((E_2 - E_1)\) trigger the electron to undergo the transition. Under normal conditions stimulated emission is not observed as the probability of spontaneous emission occurring is much higher. Spontaneous radiation emitted by a large number of atoms is incoherent because of the random nature of the emission process. In contrast stimulated emission results in coherent radiation as the waves associated with the stimulating and stimulated photons have identical frequencies, are in phase and have the same state of polarisation [7].
Therefore, with stimulated emission the amplitude of an incident wave can grow as it passes through a collection of atoms, i.e. the wave is amplified.

The process of stimulated emission competes with the processes of spontaneous emission and absorption. To amplify a beam of light by stimulated emission the rate of this process must, therefore, be increased compared to the other two processes. To achieve this for a given pair of energy levels both the number of photons of the correct frequency and the population density of the upper level $N_2$ in relation to the population density of the lower level $N_1$ must be increased. It can be shown that a necessary condition for laser action is [7]

$$N_2 > \left(\frac{g_2}{g_1}\right)N_1$$

where $g_i$ is the degeneracy of the $i$th level. For a system in thermal equilibrium $N_1 > N_2$. The non thermal equilibrium condition where more atoms in the collection have energy $E_2$ than $E_1$ is called a population inversion. To create such a condition a large amount of energy must be supplied to excite atoms into the upper level $E_2$. This excitation process is called pumping.

One method of pumping is stimulated absorption; the energy levels to be used for laser action are pumped by intense irradiation of the system. With a two level system the probabilities of stimulated emission and stimulated absorption become equal so the best that can be achieved is $N_2 = N_1$. It is, therefore, necessary to use materials with either a three or four level system. Consider the three level system shown in figure 2.8. Initially the distribution has $N_0 > N_1 > N_2$. Intense illumination of the atoms can excite
electrons from level $E_0$ into the level $E_2$. From $E_2$ the electrons decay by nonradiative processes to level $E_1$ and eventually a population inversion is created between $E_1$ and the ground state.

![Energy Levels](image)

Figure 2.8: Population of the energy levels of a three level system.

Ideally, the transition from $E_2$ to $E_1$ should be rapid so that there are always vacant states at $E_2$. The transition from $E_1$ to $E_0$ should be very slow, i.e. $E_1$ is a metastable state, to allow the build up of atoms in $E_1$ since the probability of spontaneous emission is small. The level $E_2$ should consist of a large number of closely spaced levels to use as wide a part of the spectral range of the pumping radiation as possible. Even so a three level system such as a ruby laser requires high pumping powers as the final level of the laser transition is the ground state. This means that more than half of the ground state atoms have to be pumped to the upper level to obtain a population inversion.

A four level system, such as the one shown in figure 2.9, is more efficient. Provided $E_1-E_0$ is large compared to the thermal energy at the operation temperature, the populations of the levels $E_1$, $E_2$ and $E_3$ are very small in conditions of thermal equilibrium. A population inversion can be created very quickly between levels $E_2$ and $E_1$ by pumping the atoms from the ground state to $E_3$, from which they decay rapidly to the metastable state $E_2$. In addition to optical pumping, pumping can be achieved in an electrical discharge, by electron bombardment, by the release of chemical energy or by the passage of current. The energy systems of the materials used in lasers are often complex but can usually be approximated to a three or four level system.

The gain medium of a laser is placed between a pair of mirrors which form an optical cavity. The initial stimulus is provided by spontaneous transitions between the
appropriate energy levels which result in the emission of photons travelling along the axis of the system. The signal is amplified as it travels through the medium and is ‘fed back’ by the mirrors. Saturation is reached when the gain supplied by the medium exactly matches the losses incurred in a complete round trip [7]. The gain per unit length in most active materials is usually so small that very little amplification of a light beam results from a single pass through the material. However, when the material is placed within a cavity the multiple passes that a beam makes can result in substantial amplification. One of the mirrors is made as reflective as possible, often by using high reflectivity multilayer dielectric coatings, while transmission from the other (which may be less than 50% reflecting) provides the useful output.

In summary the basic requirements which must be satisfied for laser operation are:

- There must be an active medium which emits radiation in the appropriate region of the electromagnetic spectrum.

- A population inversion must be created within this medium. The energy levels associated with the lasing transition must be suitable for pumping.

- For true laser operation there must be optical feedback at the ends of the medium to form a resonant cavity.

Figure 2.9: Population of the energy levels in a four level system.
2.3.2 Properties of Laser Radiation

Laser radiation has properties which make it suitable for a wide variety of applications including drilling, welding, holography, photochemistry, ophthalmology and interferometry. The most important properties are [7]: directionality, linewidth, coherence, brightness and tunability;

*Directionality* - With the exception of semiconductor lasers, lasers emit radiation in a highly directional, collimated beam with a low angle of divergence. This means that the energy in the laser beam can be easily collected and focused onto a small area. A conventional source emits energy into a solid angle of $4\pi$ sr making efficient collection and focusing almost impossible. With laser radiation the angle of divergence is so small that the energy can be efficiently collected even at large distances from the laser. The beam divergence is determined by diffraction. At the diffraction limit the angle of divergence in radians is given by

$$\theta = \kappa \frac{\lambda}{D}$$

where $D$ is the diameter of the aperture through which the beam emerges, and $\kappa$ is a numerical factor (close to unity) dependent on the nature of the beam. The beam divergence tends to increase with increasing power. The highly directional nature of laser beams, in particular gas laser beams, means that the laser can be used in applications which require accurate alignment such as tunnel boring and surveying. By focusing a laser beam into a small area high irradiances can be obtained which are sufficient for many drilling, cutting and welding applications. The selection of a laser for a particular application involving 'laser heating' depends on the nature of the application. For cutting applications a continuous laser might be appropriate; CO$_2$ lasers can supply a continuous output of up to 100 kW. For welding applications a pulsed laser may be more suitable; because of the short pulse duration Q-switched Nd:glass lasers are capable of generating pulses with a peak power of $10^{11}$ W.

*Linewidth* - Laser radiation can be extremely monochromatic. The output of a laser actually consists of a number of discrete frequency components (or very narrow spectral lines) as a result of standing wave patterns which are set up within the optical cavity. These frequency components are known as longitudinal, or axial, modes. The greatest possible spectral purity is achieved by operating the laser in a single mode. The high spectral purity of laser radiation (linewidths of only 1 Hz have been achieved
Chapter 2: A Comparative Study of Laser Cleaning

[7]) leads to applications in basic scientific research, e.g. photochemistry, and also in communications.

**Coherence** - Laser radiation has a high degree of spatial and temporal coherence, i.e. light at different points transverse to the direction of propagation of the beam and along the beam has a fixed phase relationship [7]. The coherence of the output from continuous gas lasers can be very high. A high degree of coherence is important in applications where the laser beam is split up. Such applications include interferometric measurement of distance and deformation where the light is split into parts which traverse different distances.

**Brightness** - Lasers have a higher brightness than any other light source. Brightness is defined as the power emitted per unit area per unit solid angle (Wm⁻²sr⁻¹) where the solid angle is that defined by the cone into which the beam spreads. A laser can emit very high levels of power in a well-collimated beam, providing a source of great brightness. Typical values of brightness are 10¹⁰ Wm⁻²sr⁻¹ for a HeNe laser and 10¹⁶ Wm⁻²sr⁻¹ for a Q-switched ruby laser. The brightness of the sun is only about 1.3 x 10⁶ Wm⁻²sr⁻¹. High brightness is important for the delivery of high power per unit area to a target.

**Tunability** - Some lasers can be tuned to emit radiation over a range of wavelengths. Dye lasers can be tuned over a large region of the visible spectrum and can often be modified to emit in the ultraviolet. The ability to tune a laser leads to applications in photochemistry and high resolution spectroscopy.

2.3.3 Reflection of Radiation

In order to understand the mechanisms by which laser radiation selectively removes layers of dirt from a stone surface it is helpful to know how much of the incident radiation is actually absorbed by the surface. If the fraction of radiation reflected from the surface, R, is known then assuming no transmission the fraction of incident radiation which is absorbed, A, can be calculated from

\[ A = 1 - R \]

The nature of reflected radiation depends on the nature of the incident beam and on the optical properties of the medium being considered. A specular reflecting medium, such
as a mirror, reflects the beam in one direction only which can, therefore, be easily
detected and measured. A dull surface, however, scatters the beam in many directions
making measurement difficult.

2.3.3.1 Specular Reflection

Specular reflection occurs to a certain extent at all surfaces which constitute the
boundaries of condensed phases [8]. Consider the situation shown in figure 2.10.
Electromagnetic radiation is incident at an interface between two media. A part of the
beam is reflected back into medium 1, while part continues into medium 2 and is
refracted.

\[
R = \frac{I}{I_0} = \frac{(n - 1)^2 + n^2 k^2}{(n + 1)^2 + n^2 k^2}
\]

where \( R \) is reflectivity
\( I_0 \) is incident intensity
\( I \) is reflected intensity
\( n = n_2 / n_1 \) is relative refractive index
\( k \) is absorption index defined through Lambert's law: \( I = I_0 \exp[-4\pi nk d/\lambda_0] \)
where \( d \) is thickness of reflecting layer

\[ \lambda_0 \] is wavelength of radiation in vacuum

For an air/glass interface with \( n = 1.5 \) and \( k \) negligible the reflectivity at normal incidence is about 4%. If \( n \) and \( k \) are unknown then by measuring the intensity of radiation reflected at an angle \( \theta \), and comparing to the incident intensity it is possible to calculate the reflectivity \( R \) and hence the fraction of incident radiation absorbed by the second medium.

### 2.3.3.2 Diffuse Reflection

Reflection from a matt, or dull, surface is distinct from reflection at a smooth interface of dielectric media in that it depends more directly on the particulate nature of the medium being considered. The radiation reflected from such media can be regarded as consisting of two parts [8]:

(i) The *regular reflection* (sometimes known as surface or mirror reflection) which is of the same nature as the specular reflection discussed in the previous section and, therefore, governed by the Fresnel equations.

(ii) The *diffuse reflection* is a result of penetration of a fraction of the incident radiation into the interior of the sample. A part of this radiation is returned to the surface of the sample following partial absorption and multiple scattering at the boundaries of the individual particles of which the sample is composed.

All formulae for diffuse reflection incorporate the Lambert cosine law in one form or another which has been phenomenologically formulated from the observation that a matt surface irradiated with constant intensity appears uniformly light at all angles of observation. It has been suggested that an ideally diffuse reflecting substance would obey

\[
I_{\text{obs}} = I_0 \cos(\alpha) \cos(\theta)
\]

where:

- \( I_0 \) is incident intensity
- \( I_{\text{obs}} \) is reflected intensity
- \( \alpha \) is angle of incidence
- \( \theta \) is angle of observation
and have the characteristics illustrated in figure 2.11 [9].

![Figure 2.11: Distribution of reflected radiation from an ideally diffuse reflecting substance.](image)

According to the cosine law the reflected radiation is distributed symmetrically with respect to the surface normal, irrespective of the angle of incidence. The distribution of reflected radiation is, thus, spherical. Research has shown [9] that the Lambert cosine law is strictly valid only for small values of $\theta$ and $\alpha$. For larger values deviations do occur, especially in absorbing materials, which are more pronounced when the irradiance and observation planes do not coincide. In such cases the distribution tends toward an oblate ellipsoid [8]. Several theories have been put forward to explain these observations:

(i) By assuming a matt surface to be composed of small crystallites statistically distributed at all possible angles to the macroscopic surface, the combined specular reflections from all such surfaces give rise to the scattering of the incident radiation.

(ii) Multiple scattering by individual particles within the interior of the sample is responsible for the diffusion of light.

The second explanation is considered to be more plausible. It has also been suggested that both regular and diffuse reflection parts are always present, the relative proportion of each being dependent on the nature of the reflecting medium. In order to calculate the fraction of incident radiation absorbed by a matt surface the total amount of radiation diffusely reflected from the surface must first be measured. A convenient method of making such a measurement is to use an integrating sphere.
2.3.3.3 Measurement of Reflected Radiation Using an Integrating Sphere

An integrating sphere is a hollow enclosure with walls constructed of a material which diffusely reflects radiation of all wavelengths of interest efficiently. The intensity at any part of the sphere due to reflected radiation is a measure of the total reflected radiation from a particular source, independent of the spatial distribution or of the location of the source on the sphere. This result can be proved in the following manner [8]:

Consider a small element of surface \( dA \). Assume the surface to be an ideal diffuser so that the radiant flux \( B \) can be taken to be the same in all directions. A small element of the surface \( dA_2 \) is irradiated by \( dA_1 \) as shown in figure 2.12.

![Figure 2.12: Two elements of a surface; \( dA_2 \) is irradiated by \( dA_1 \).](image)

The radiant intensity of \( dA_1 \) in direction \( \theta_1 \), i.e. the flux emitted per unit solid angle, is \( BdA_1 \cos \theta_1 \). The solid angle subtended by \( dA_2 \) at \( dA_1 \) is \( (dA_2 \cos \theta_2)/d^2 \). The total flux received by \( dA_2 \) from \( dA_1 \) is therefore given by:

\[
\frac{BdA_1 dA_2 \cos \theta_1 \cos \theta_2}{d^2}
\]

Now consider \( dA_1 \) and \( dA_2 \) to be elements of a sphere, centre \( C \), radius \( r \), as shown in figure 2.13. It has been assumed that there is a light source within the sphere so that the radiant flux emanating from \( dA_1 \) is a result of a reflection process. The flux received at \( dA_2 \) from \( dA_1 \) is:

\[
\frac{BdA_1 dA_2 \cos^2 \theta}{d^2}
\]

But \( \cos \theta = d/2r \) so the flux received at \( dA_2 \) becomes
For a given surface element $dA_1$, the flux received by $dA_2$ is therefore independent of its position on the sphere. In other words, the flux reflected from each part of the sphere is equally distributed over the other parts. The flux measured at any point on the sphere depends only on the total enclosed flux.

Experimentally, the total enclosed flux is that obtained by reflection from a sample surface. Reflectivity measurements using an integrating sphere are often made by the substitution method, illustrated in figure 2.14.
Radiation from an external source enters the integrating sphere through aperture 1 and falls on the sample surface at 2. The radiation intensity at the sphere wall is measured by a detector at aperture 3. The sample is then replaced with a standard and the measurement repeated. The relative value of the intensity measured at 3 is used as a measure of the reflectivity of the sample relative to the standard.

Due to the finite size of the apertures in the integrating sphere deviations from ideal behaviour do occur [8]. These can be illustrated by considering a sphere of radius $R$ with an entrance port through which a sample is irradiated with a constant radiation flux $P$ at a fixed angle of incidence. The area of the exit port through which the measurements are made is $b$. The flux which passes through this port due to direct reflection by the sample is

$$B_{0s} = \frac{PR_s b}{S}$$

where $S$ is the total area of the sphere and $R_s$ is the reflectivity of the sample. Multiple reflections from the inner surface of the sphere contribute to the total flux at the exit port. Let $R_{av}$ be the average reflectivity of the entire sphere wall, including entrance and exit ports as well as the sample. Since the intensity of radiation reflected from a given source has been shown to be uniform throughout the wall, the flux which is reflected once by the sphere wall before leaving the sphere is given by

$$B_{1s} = \frac{PR_s R_{av} b}{S}$$

Similarly, for two reflections

$$B_{2s} = \frac{PR_s R_{av}^2 b}{S}$$

The total flux at the exit port is, therefore, given by

$$B_s = \sum_{i=0}^{\infty} B_{is} = \frac{PR_s b}{S} \left(1 + R_{av} + R_{av}^2 + R_{av}^3 + \ldots \right)$$

which can be summed to give
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\[
B_s = \frac{PR_s b}{S(1 - R_{sv})} = PR_s \eta_s
\]

where \( \eta_s = \frac{b}{S(1 - R_{sv})} \) is called the sphere efficiency. Assuming the entrance and exit ports of the sphere to have zero reflectivity then the average reflectivity of the sphere wall is the weighted average of the reflectivities of the sample and sphere wall:

\[
R_{av} = \frac{R_s c + R(4\pi r^2 - a - b - c)}{4\pi r^2}
\]

where \( R \) is the reflectivity of the sphere wall, \( c \) is the area of the sample port and \( a \) is the area of the entrance port. Using \( S = 4\pi r^2 \),

\[
R_{av} = \frac{1}{S}(R_d + R_s c)
\]

where \( d = S-a-b-c \). When the sample is replaced by the standard a similar expression is obtained for the flux received through \( b \):

\[
B_{st} = \frac{PR_{st} b}{S(1 - R_{sv})} = PR_{st} \eta_{st}
\]

where \( R_{st} \) is the reflectivity of the standard and

\[
R_{av} = \frac{1}{S}(R_d + R_{st} c)
\]

The ratio of the two measured fluxes is then given by

\[
\frac{B_s}{B_{st}} = \frac{R_s \eta_s}{R_{st} \eta_{st}}
\]

and the ratio of the sphere efficiencies by:
The sphere error $\alpha$ which is a result of the different efficiencies of the sphere when the sample and standard are used, is defined as

$$\alpha = \frac{\eta_s}{\eta_{st}} - 1$$

The sphere error is small in cases where the sample and standard are approximately equal, and the relative reflectivity is simply $B_{st}/B_{st}$. If the sample and standard have very different reflectivities the sphere error can be reduced by making the sample port small compared to the total surface of the sphere.

### 2.3.4 Experimentation

A qualitative analysis of the effects of four pulsed lasers (with outputs ranging from the ultraviolet to the infrared) on polluted limestone has been made. The lasers used were CO$_2$, liquid dye, excimer and Nd:YAG. In some cases tests were also carried out on polluted sandstone and aluminium. Included in the work with the CO$_2$ and Nd:YAG lasers was a quantitative analysis of the absorption of radiation by both clean and polluted stone surfaces. After completion of this work a spectrophotometer with an integrating sphere attachment became available and was used to provide reflectivity measurements between 190 nm and 1100 nm for a number of stone samples. The configuration of the dye and Nd:YAG lasers is also described.

#### 2.3.4.1 CO$_2$ Laser Radiation

**Effects on Polluted Limestone**

The effects of CO$_2$ laser radiation on polluted limestone were studied [10]. A Laser Applications Ltd. transversely excited atmospheric CO$_2$ laser provided up to 4 J of energy in pulses of 100 ns duration at a wavelength of 10.6 $\mu$m, i.e. in the far infrared part of the electromagnetic spectrum. The output was rectangular in cross-section (3.0 cm x 3.5 cm). A ZnSe lens was used to focus the beam onto the sample. The sample, a piece of Lincoln limestone with a black pollution crust approximately 0.2 mm thick,
was initially placed beyond the focal point of the lens, as shown schematically in figure 2.15.

![Figure 2.15: Schematic representation of the experimental arrangement.](image)

The beam was passed through a circular aperture 2.5 cm in diameter to provide a circular beam profile. This reduced the energy per pulse by 50%. Three sheets of perspex were used as attenuators and to protect the lens from debris. Each attenuator transmitted 65% of the incident energy so by the time the beam reached the sample it had been reduced to approximately 0.5 J. The sample was moved towards the lens, thereby increasing the incident energy density, in steps of 1.0 cm. At each distance the sample was exposed to a maximum of 100 pulses at a repetition rate of 0.4 Hz. The size of the laser beam was measured from an outline of the beam obtained on thermal paper placed over the surface of the sample at each appropriate distance. The effects of irradiation were observed directly by eye and more closely through a stereomicroscope (magnification x20 and x60).

The results are summarised in table 2.1. Fluence is the energy density (Jcm\(^{-2}\)) of the laser beam on the sample surface. A fluence of 0.5 Jcm\(^{-2}\) was sufficient to remove very small amounts of material which could not be detected by eye. Evidence for this is the sparks formed during the interaction. However, even 100 pulses were insufficient to produce a cleaning effect. The fluence had to be increased by a factor of 10 before cleaning was observed. The black crust was then removed at an approximate rate of 0.01 mm per pulse. Figure 2.16 shows an area of the black crust which has been exposed to 20 pulses at 5 Jcm\(^{-2}\). The laser beam was 3.5 mm in diameter and dirt has been removed completely from an area approximately 2.0 mm in diameter. This suggests that more energy is contained in the central portion of the focused laser beam, assuming the crust to be of uniform thickness over the area of interest. It should be noted that the values of fluence calculated here are average values and not peak values.
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<table>
<thead>
<tr>
<th>Fluence / Jcm^{-2} (± 10%)</th>
<th>Effect on Polluted Stone Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.5</td>
<td>None</td>
</tr>
<tr>
<td>0.5</td>
<td>Bright sparks visible during interaction. No visible removal of dirt.</td>
</tr>
<tr>
<td>1.3</td>
<td>Increased density of sparks. Still no visible removal of dirt</td>
</tr>
<tr>
<td>5.0</td>
<td>Bright plasma formed during interaction, accompanied by loud 'snapping' sound. Dirt particles ejected from surface. 5-10 pulses sufficient to remove complete thickness of dirt and expose underlying stone.</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of the effect of increase in fluence on the removal of dirt from a polluted limestone surface.

A larger area (10.0 mm x 15.0 mm) of the surface was cleaned using an x-y table to raster the area with a repetition rate of 1 Hz at 5 Jcm^{-2}. The beam size was 3.5 mm. Three pulses were fired every 1 mm. A close-up of the irradiated area is shown in figure 2.16.

Figure 2.16: Area of black crust exposed to 20 pulses at 5 Jcm^{-2}. Magnification x15.
figure 2.17. Most of the crust has been removed but in some parts dirt remains. This is due in part to the table being moved manually, so some areas received more pulses than others. However, the thickness of the crust is bound to vary over such an area and it appears as if some areas received insufficient pulses to remove the crust completely. On closer inspection it is apparent that the interaction has damaged the underlying stone. The cleaned area appears very rough with dirt remaining in some places and stone material having been removed from areas which have been over-irradiated. In certain areas the surface has a nodular texture with thin 'stalagmites' (< 0.1 mm in cross-section) of stone protruding upwards, often topped by a globule of dirt which appears to have been melted and resolidified. From these results it seems as if CO₂ laser radiation is unable to clean selectively; once the black crust has been removed the radiation continues to interact with and modify the surface of the underlying stone.

![Figure 2.17: CO₂ laser cleaned area. Magnification x10.](image)

**Effects on Clean Stone**

A clean, smooth surface of Lincoln limestone was exposed to a total of 100 pulses at 5 Jcm⁻². The laser beam was focused to a diameter of 3.5 mm. After 5 pulses the stone was removed and photographed. It was then replaced in the same position and irradiated further. The process was repeated for 10, 15, 20, 50 and 100 pulses.
The results showed that after only 5 pulses damage to the surface was evident; stone had been removed from the centre of the irradiated area leaving a small crater approximately 1.5 mm across. Further irradiation accentuated the damage, deepening the crater. Figure 2.18 clearly shows the damage caused to the surface by 10 pulses. Damage can also be seen on the lower line, as a result of error in replacement of the sample.

![Surface prior to irradiation](image1) ![Surface after irradiation](image2)

Figure 2.18: Damage caused to a clean limestone surface by CO\textsubscript{2} radiation. The crater in the centre resulted from 10 pulses at 5 Jcm\textsuperscript{-2}. Magnification x10.

These results clearly demonstrate that irradiation of a clean stone surface at a fluence which is sufficient to remove layers of dirt leads to damage of the surface. This suggests that laser radiation at 10.6 \textmu m is unable to distinguish sufficiently between the black crust to be removed and the underlying limestone for the process to be self-limiting. Once the crust has been removed further pulses continue to interact with and remove material from the stone itself.

**Absorption Measurements**

The aim of this work was to obtain quantitative results for the relative absorption properties of clean and polluted limestone surfaces at 10.6 \textmu m. Experiments were
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Initially carried out to investigate the distribution of reflected radiation from samples of limestone. A schematic representation of the experimental arrangement is shown in figure 2.19.

Figure 2.19: Schematic representation of the experimental arrangement for measurement of the reflected radiation distribution from a stone surface.

The angle of incidence, $i$, was kept constant at $-20^\circ$ and the intensity of reflected radiation was measured by a pyroelectric detector in steps of $10^\circ$. Energy absorbed by the ferroelectric material of the detector causes a variation in its spontaneous polarisation which induces a voltage change that can be detected, the amplitude of which can be measured on an oscilloscope [7]. No measurements could be made between $0^\circ$ and $-40^\circ$ due to the experimental arrangement. At each angle five measurements were taken and the results averaged before being plotted on a polar diagram of intensity versus angle of observation, $j$. All measurements were made in the plane of incidence of the laser pulse. A spot of approximately 3.5 mm diameter was irradiated at a fluence of only $0.3 \text{ Jcm}^{-2}$ to ensure there was no modification to the surface of the sample. The experiment was carried out on several samples including clean and polluted limestone (Lincoln and Ancaster) and perspex.
The results show that the distribution of reflected radiation from the samples of limestone, both clean and polluted, is approximately circular. Figures 2.20 and 2.21 show typical results for clean and polluted surfaces with a 'rough' texture. The irradiated area had an approximate surface roughness of less than 0.5 mm. Similar results were obtained at an incident angle of $i = +20^\circ$. Figure 2.22 shows the distribution for a relatively flat surface (roughness less than 0.1 mm) on the same sample of Ancaster limestone. The distribution is not as circular, with a slightly pronounced specular component. Figure 2.23 shows, for comparison, the distribution obtained from a flat perspex surface which has a very strong specular component and virtually no diffuse characteristics.

![Incident beam](image)

Figure 2.20: Distribution of reflected radiation from 'rough' clean Ancaster limestone.

These results have shown that the distribution of reflected radiation from a stone surface irradiated at 10.6 $\mu$m can be approximated to the circular distribution associated with an ideal diffuse reflecting surface. This appears to apply equally to both clean and polluted limestone surfaces. However, it should be noted that for a relatively 'flat' stone surface an increased specular component was present. There appears to be some dependence of the diffuse reflecting nature of the stone surface on its apparent 'smoothness'. For the purpose of the relative absorption measurements of clean and

---

1 Note: On polar diagrams $0^\circ$ corresponds to $+90^\circ$ and $180^\circ$ corresponds to $-90^\circ$ in the experimental arrangement shown in figure 2.19.
Figure 2.21: Distribution of reflected radiation from a 'rough' polluted surface of Ancaster limestone. The polluted surface is a thin grey crust approximately 0.1 mm thick.

Figure 2.22: Distribution of reflected radiation from a 'flat' clean surface of Ancaster limestone.
polluted limestone it is assumed that the surfaces of interest reflect radiation diffusely in accordance with the Lambert cosine law.

An integrating sphere has been used to measure the relative intensities of radiation reflected from clean and polluted limestone surfaces. Integrating spheres have been used previously to make reflectivity measurements in the infrared [9, 11-12].

An integrating sphere was constructed from aluminium foil (approximately 98% reflecting at 10.6 μm). The foil was screwed up and unfolded so that its creased surface approximated a diffuse reflecting substance and then moulded into a sphere 20 cm in diameter. The distribution of reflected radiation from a 'creased' surface of aluminium foil has been measured at normal incidence and is shown in figure 2.24. The distribution is composed of multiple specular components but for the purpose of this work can be assumed to be diffuse. Entrance and sample ports were made 3 cm in diameter, opposite each other. An exit port was made 1 cm in diameter. A schematic representation of the experimental arrangement is shown in figure 2.25.
Figure 2.24: Distribution of reflected radiation from 'creased' aluminium foil.

Figure 2.25: Schematic representation of the experimental arrangement for relative reflectivity measurements.
The substitution method was used to measure the reflectivities of several clean and polluted limestone surfaces (Lincoln and Ancaster) relative to an aluminium standard. The surface of each sample was irradiated at normal incidence by a beam 3.5 mm in diameter with a fluence of 0.3 J cm\(^{-2}\). The radiation reflected through the exit port was measured on an oscilloscope via a pyroelectric detector. The surface of the stone was exposed to 50 pulses with the laser firing continually at a repetition rate of 1 Hz. The voltage signals received from the detector were averaged so that any fluctuations in the laser output energy (±5%) became unimportant when comparing readings for different samples. The experiment was repeated at 5 areas on each surface. The standard used was a piece of aluminium foil which had been creased in the same way as the walls of the sphere. Measurements were also repeated with the detector positioned at an exit aperture on the opposite side of the sphere. It was found that readings varied by less than 10%. A summary of the results is given in table 2.2. \(B_s\) is the average reflected intensity measured by the detector for a stone surface and \(B_{st}\) is the intensity measured for the standard.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clean/Polluted</th>
<th>Mean (B_s/B_{st}) (±10%)</th>
<th>Mean (R_s/R_{st}) (±10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lincoln 1</td>
<td>Clean</td>
<td>0.024</td>
<td>0.029</td>
</tr>
<tr>
<td></td>
<td>Polluted(^1)</td>
<td>0.023</td>
<td>0.028</td>
</tr>
<tr>
<td>Lincoln 2</td>
<td>Polluted(^2)</td>
<td>0.014</td>
<td>0.017</td>
</tr>
<tr>
<td>Ancaster 1</td>
<td>Clean</td>
<td>0.049</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>Polluted(^3)</td>
<td>0.026</td>
<td>0.031</td>
</tr>
<tr>
<td>Ancaster 2</td>
<td>Clean</td>
<td>0.045</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>Polluted(^3)</td>
<td>0.027</td>
<td>0.032</td>
</tr>
</tbody>
</table>

All clean surfaces were flat to about 0.1 mm.

\(^1\) Thin light grey pollution crust ~0.1 mm thick.
\(^2\) Black pollution crust ~0.5 mm thick.
\(^3\) Grey pollution crust ~0.1 mm thick, flat to ~0.5 mm.

Table 2.2: Relative reflectivities of limestone surfaces measured at 10.6 \(\mu\)m.

\(R_s/R_{st}\) is the reflectivity of the stone surface relative to the aluminium standard. The values shown in table 2.2 are maximum average values calculated from
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\[
\frac{R_s}{R_{st}} = \frac{\eta_s}{\eta_{st}} \frac{B_s}{B_{st}}
\]

where \( \eta_s/\eta_{st} \) is the ratio of the sphere efficiencies. A maximum value for \( \eta_s/\eta_{st} \) of 1.2 has been calculated assuming the reflectivities of the standard and sample to be 100% and 0% respectively.

The results show that, in general, polluted surfaces absorb slightly more radiation than clean limestone surfaces at 10.6 \( \mu \)m. However, the difference which has been measured of only a few % confirms the view that \( \text{CO}_2 \) radiation is unable to remove polluted layers from limestone selectively. Relative to the standard, the clean surfaces which were measured reflected between 2.9% and 5.9% of the incident radiation while polluted surfaces reflected between 1.7% and 3.2%. It must be remembered that the aluminium surface of the sphere only roughly approximates the highly reflecting and diffuse characteristics of an ideal sphere wall. Absolute values of reflectivity should, therefore, be treated with caution. However, comparison between the relative reflectivities of clean and polluted surfaces has shown that the \( \text{CO}_2 \) laser would not be a suitable tool for the cleaning of polluted limestone sculpture. Since the underlying stone absorbs a large proportion of the incident radiation, further irradiation once the dirt has been removed would lead to damage, as has already been seen in figure 2.18. However, \( \text{CO}_2 \) radiation might be more suitable for the cleaning of highly reflecting metal objects. Figure 2.26 shows part of an aluminium (98% reflecting at 10.6 \( \mu \)m) printing press covered by a mixture of ultraviolet resins and dyes. An area of the press (1.0 cm x 2.0 cm) has been cleaned by \( \text{CO}_2 \) radiation. Between 10 and 20 pulses at a fluence of approximately 10 Jcm\(^{-2}\) were sufficient to clean an area approximately 5 mm in diameter. The dirt has been completely removed from the irradiated area leaving a smooth aluminium surface with no visible signs of damage.

2.3.4.2 Liquid Dye Laser Radiation

A pulsed dye laser operating in the yellow part of the electromagnetic spectrum has been acquired from University College Hospital in London. The laser was reassembled and aligned at Loughborough and tested on samples of polluted limestone and sandstone.
Figure 2.26: Area of an aluminium printing press cleaned by CO₂ laser radiation. Magnification x1.5.

Configuration of the Laser
A dye laser is essentially a four level system with the active medium being an organic dye dissolved in a solvent [7]. When the dye is excited by short wavelength radiation it emits radiation at a longer wavelength, i.e. the dye fluoresces. All dye lasers are optically pumped. The choice of the pump source depends on the absorption spectrum of the dye and the output desired. Commercial methods include flashlamps, nitrogen lasers, solid state lasers and ion lasers.

The basic layout of the dye laser used in the initial tests is shown schematically in figure 2.27. The dye is circulated through a cell and pumped by two linear xenon flashlamps inside a highly reflecting elliptical cavity. The laser output is through a mirror which reflects 42.5% at 590 nm. The firing circuit for the flashlamps is shown in figure 2.28. A high voltage supply charges two capacitors, $C_1$ and $C_2$, to a voltage $V$. The thyratron acts as a very fast switch. When a short voltage pulse (700V) is applied to the grid of the thyratron (A) an arc discharge is created between the anode and cathode and the thyratron conducts [13]. At the same time the flashlamps are triggered by an external circuit and the capacitors discharge through the tubes. Resistances $R_2$
and $R_3$ (19.8 kΩ) limit the current flowing through the flashlamps and also prevent both capacitors from discharging through the same lamp.

Figure 2.27: Schematic representation of the basic layout of the dye laser.

Figure 2.28: Flashlamp firing circuit.
The mirrors forming the optical cavity were aligned using a 15 mW HeNe laser:

(i) Initially, the HeNe was aligned with the dye cell.

(ii) The output mirror was positioned at the opposite end of the dye cell to the HeNe, and adjusted until the reflected spot fell on the output aperture of the HeNe.

(iii) The 100% reflecting mirror was positioned between the HeNe and the dye cell and adjusted as in (ii).

(iv) Finally, the output energy was monitored using a calorimeter and maximised by making small adjustments to the mirrors.

The active medium of the laser was a 0.8M solution of rhodamine 6G in methanol, which was maintained at a temperature of 21°C. The dye fluoresces over the range 553-615 nm with a peak output at 590 nm. The laser provided up to 200 mJ in pulses of 2 μs duration (measured as full width half maximum FWHM). It was possible to control the output energy of the laser by varying the voltage applied to the flashlamps. Figure 2.29 shows a graph of output energy versus flashlamp voltage. A maximum efficiency (output energy/input energy) of approximately 0.1% was achieved at a maximum voltage of 15 kV.

![Figure 2.29: Output energy as a function of flashlamp voltage.](image)
Effects on Polluted Limestone

The effects of dye laser radiation on surfaces of limestone composed of (i) a black pollution crust and (ii) green lichen have been qualitatively studied. A planoconvex lens was used to focus the laser beam into an area 1.5 mm in diameter on the sample surface. The output energy of the laser was slowly increased until an effect was observed. The results are summarised in table 2.3.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Fluence / Jcm^{-2} (±10%)</th>
<th>Effect on Polluted Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black pollution crust on limestone sculpture from Lincoln. Crust ~0.1 mm thick over irradiated area.</td>
<td>4.0</td>
<td>Lightening of the surface after 1 pulse. 20 pulses required to remove dirt completely from an area 1.5 mm in diameter.</td>
</tr>
<tr>
<td>Green layer of lichen &lt; 0.1 mm thick on quarried limestone.</td>
<td>2.0</td>
<td>Slight lightening of surface, but fluence insufficient to clean area, even after 50 pulses.</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>1 pulse appeared to remove lichen from an area 1.75 mm in diameter. 5 pulses cleaned an area 2.00 mm in diameter, while further irradiation appeared to leave stone undamaged.</td>
</tr>
</tbody>
</table>

Table 2.3: Effect of dye laser radiation on polluted limestone surfaces.

Figure 2.30 shows an area (3.0 mm × 5.0 mm) of the black crust which has been cleaned at a fluence of 4.0 Jcm^{-2}. The number of pulses required to remove the crust completely was dependent on its thickness, which varied between 0.1 mm and 0.5 mm. The area was cleaned in 1 hour. This was due to the slow repetition rate of the laser (less than 0.1 Hz), which was limited by there being no cooling for the flashlamps.
Figure 2.30: Laser cleaned area on polluted limestone from Lincoln Cathedral. Magnification ×4.

Figure 2.31 shows an area (10.0 mm × 8.0 mm) of the limestone surface from which lichen appears to have been removed. Cleaning took approximately 20 minutes at 11 Jcm⁻².

Figure 2.31: Laser-cleaned area on limestone surface covered by lichen. Magnification ×3.
On both samples of limestone surface deposits appear to have been successfully removed without damage to the underlying stone. In the case of the lichen, surface analysis techniques would be required to verify that the lichen has actually been removed and not simply discoloured.

**Effects on Clean Stone**

A clean surface of Ancaster limestone was exposed to 20 pulses at 5.5 Jcm\(^{-2}\). Figure 2.32 shows the result. The irradiated area (within the marked square) has darkened slightly, but otherwise appears to be undamaged. The results show that dye laser radiation appears to remove polluted layers more selectively than CO\(_2\) radiation. However, with the relatively long pulse length (2 \(\mu\)s) overcleaning at high fluence might lead to thermal-induced damage. The dye laser also has the disadvantages of a relatively slow repetition rate and contact with harmful chemicals; many of the dyes are known to be carcinogenic.

![Surface prior to irradiation](image1.png) ![Surface after irradiation](image2.png)

Figure 2.32: Effects of dye laser radiation on a clean limestone surface. Magnification \(\times 7\).

**Effects on Sandstone**

The effects of dye laser radiation on two types of sandstone from Glasgow have been briefly studied:

(i) A red sandstone from the south of Scotland composed mainly of grains of silica with an iron oxide coating and a high porosity.
(ii) A blonde sandstone comprising silica cemented by carbonates, clays and iron oxides and with a lower porosity.

The results are summarised in table 2.4.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Fluence / Jcm⁻²</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polluted red sandstone¹</td>
<td>6.0</td>
<td>3 pulses sufficient to remove most of crust from an area 1.5 mm in diameter. Surface left with a dull brown appearance. Some dirt remained as grey powder (burnt) and some as shiny black globules.</td>
</tr>
<tr>
<td>Clean red sandstone</td>
<td>6.0</td>
<td>3 pulses turned surface from red to a dirty white colour. Individual grains appeared opaque and colourless.</td>
</tr>
<tr>
<td>Polluted blonde sandstone²</td>
<td>6.0</td>
<td>5 pulses sufficient to remove most of crust from area 1.5 mm in diameter. Some dirt remaining as powder between grains and some as globules fused to grains. Surface appears a grey-white colour.</td>
</tr>
<tr>
<td>Clean blonde sandstone</td>
<td>6.0</td>
<td>5 pulses turned the irradiated area a darker colour, giving the surface a light grey appearance.</td>
</tr>
</tbody>
</table>

¹ Thin black pollution crust ~ 0.1 mm thick.
² Thin grey pollution crust ~ 0.1 mm thick.

Table 2.4: Effects of dye laser radiation on polluted sandstone.
Radiation at 590 nm appears to be unable to selectively remove pollution layers from red and blonde sandstones without modifying the underlying stone. At 6.0 Jcm\(^{-2}\) most of the irradiated crust can be removed. However, some remains in grey powder form between the grains and some appears to have been partially melted and fused to adjacent grains in shiny black globular form. At 6.0 Jcm\(^{-2}\) irradiation of a clean red sandstone results in a colour change of the surface. It appears as if the red iron oxide coating of the grains is removed, giving the surface a white appearance. In the case of the blonde sandstone irradiation of the clean surface results in its darkening, possibly due to the removal of the white calcitic cement. The work has shown that dye laser radiation at 590 nm is inappropriate for the cleaning of these sandstones.

### 2.3.4.3 Excimer Laser Radiation

A KrF excimer laser (Lambda Physik, EMG 200) provided radiation in the far ultraviolet part of the electromagnetic spectrum (248 nm) with a pulse length of 30 ns (FWHM). The rectangular output of the laser was brought to a focus (2.2 mm × 0.6 mm) by a convex lens, giving an average fluence of 7.6 Jcm\(^{-2}\) (peak fluence 9.0 Jcm\(^{-2}\)) at the focal plane. Tests were carried out on the two samples of polluted limestone which have already been described in section 2.3.4.2. The results are summarised in table 2.5.

The results show that radiation at 248 nm is capable of removing black dirt layers from limestone but only by a very thin layer at a time; at 5.0 Jcm\(^{-2}\) the rate of removal was approximately 0.002 mm per pulse over an area of only 0.5 mm × 2.0 mm (compared to 0.01 mm per pulse for CO\(_2\) radiation). Further irradiation of the underlying stone at 5.0 Jcm\(^{-2}\) resulted in ejection of material from the surface, which shows that the interaction is not selective. Laser radiation at 248 nm would, therefore, not be suitable for the removal of black crusts from sculpture, particularly sculpture with a friable surface. Excimer radiation appears to be more efficient in the removal of lichen. Since lichen was removed at only 2 Jcm\(^{-2}\) it was possible to expand the laser beam to clean a larger area. However, irradiation of a friable limestone surface at 2.0 Jcm\(^{-2}\) still resulted in loss of material. Again, surface analysis techniques would be required to verify the complete removal of lichen from the irradiated area. One other disadvantage of excimer lasers is the contact with corrosive gases, particularly fluorine, which over a period of time can lead to the degradation of optical components within the laser.
<table>
<thead>
<tr>
<th>Surface</th>
<th>Average Fluence / Jcm(^{-2})</th>
<th>Effect on Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black pollution crust</td>
<td>7.6</td>
<td>10 pulses at 2 Hz darkened irradiated area. 50 pulses removed crust from area 0.5 mm (\times) 2.0 mm. Clouds of material ejected from surface upon irradiation of underlying stone.</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>Area 0.5 mm (\times) 2.0 mm cleaned after 50 pulses. Underlying stone not removed to same extent.</td>
</tr>
<tr>
<td></td>
<td>&lt;5.0</td>
<td>After 500 pulses only effect observed was a slight darkening of the surface.</td>
</tr>
<tr>
<td>Green lichen</td>
<td>7.6</td>
<td>After 50 pulses lichen appeared to have been removed from an area 0.5 mm (\times) 2.0 mm.</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>50 pulses sufficient to clean area 1.0 mm (\times) 4.0 mm.</td>
</tr>
<tr>
<td>(Sample moved behind focus to reduce fluence)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean friable surface of limestone</td>
<td>2.0</td>
<td>Clouds of material ejected from surface.</td>
</tr>
</tbody>
</table>

Table 2.5: Effect of excimer laser radiation on polluted limestone surfaces.

### 2.3.4.4 Nd:YAG Laser Radiation

A pulsed Nd.YAG laser, operating at 1.06 \(\mu\)m in the near infrared part of the electromagnetic spectrum, has been reassembled and aligned. The interaction of 1.06 \(\mu\)m radiation with polluted limestone and sandstone has been studied qualitatively.
Quantitative measurements of the absorption of radiation at 1.06 μm by clean and polluted limestone, sandstone and marble surfaces have also been made.

Configuration of the Laser

The Nd:YAG laser is essentially a four level system. The active medium is yttrium aluminium garnet (Y₃Al₅O₁₂) with the rare earth metal ion neodymium Nd³⁺ present as an impurity. The Nd³⁺ ions, which are randomly distributed on lattice sites normally occupied by the yttrium ions, provide the energy levels for both the lasing transitions and pumping. A schematic representation of the J. K. Lasers Ltd. system 2000 laser is shown in figure 2.33.

![Schematic representation of the J. K. Lasers Ltd. Nd:YAG laser.](image)

The oscillator consists of a linear xenon flashlamp and a rod of the active medium inside a highly reflecting elliptical cavity, with the lamp along one focal axis and the laser rod along the other. The amplifier consists of a second laser rod which is pumped by two xenon flashlamps. Initially the Pockel's cell and intra-cavity etalon were removed and the rear mirror and output etalon aligned using a HeNe probe beam as discussed in section 2.3.4.2. The 45° mirrors were adjusted to pass the beam through the centre of the amplifier rod. The intra-cavity etalon was replaced and adjusted to give maximum energy output from the resonator. The operating temperature of the etalons was set at 40°C. A constant temperature must be maintained since the etalon-
reflectivity temperature characteristic is periodic at a given wavelength. The Pockel's cell Q-switch was replaced and aligned. The purpose of the Q-switch is to produce laser pulses of short duration (6-50 ns) and high peak power by storing energy in the laser rod for the first half of the flashlamp pulse and then releasing it [7]. This is achieved by applying a high voltage bias across the KDP crystal within the Pockel's cell. Removal of this voltage after a period set to maximise the stored laser energy allows formation of the Q-switched laser pulse. Alignment of the cell was carried out using the following procedure:

(i) A HeNe laser was aligned to the oscillator rod.

(ii) The Pockel's cell was replaced and adjusted so that the HeNe beam passed through the centre of the crystal.

(iii) One polarised plate was placed before the cell and a second (crossed to the first) placed after. A piece of white card was then positioned between the cell and the laser rod and used as a screen. The cell was adjusted until the HeNe beam fell on the centre of a Maltese cross viewed on the screen.

(iv) The laser was run fixed-Q and the rear mirror and polariser (within the Pockel's cell) were adjusted to maximise the output energy.

(v) On the Pockel's cell drive unit the bias voltage was set to 4 kV and the time delay to maximum. The bias was then set to the central value of the voltage region within which there is no lasing. The oscillator was set to 700 V and the time delay reduced to obtain maximum Q-switched output.

The duration of the laser pulse was measured as 20 ns (FWHM) Q-switched and 100 μs fixed-Q. The laser provided up to 400 mJ per pulse (multimode), with essentially a top hat profile, at a repetition rate between 0 and 25 Hz.

Effects on Limestone
The effects of Q-switched and fixed-Q Nd:YAG radiation on several polluted limestone surfaces have been studied.

Fixed-Q radiation was found to be relatively efficient in the removal of typical black encrustations from limestone surfaces. In most cases a fluence of 1 Jcm⁻² was sufficient to remove material from the crust. Each pulse led to the ejection of a cloud of material
(visible to the naked eye) from the surface, accompanied by plasma formation, a 'low' snapping sound and a burning smell. However, at 1 Jcm\(^{-2}\) there was no significant removal of dirt and no apparent alteration to the polluted surface. At higher fluence dirt was removed sufficiently to reveal the underlying limestone. On close inspection of the irradiated areas it was apparent that the relatively long duration of the laser pulse had given rise to various thermal effects. The cleaned surface was composed mainly of limestone, but with areas covered by grey powder and shiny black globules. The powder appeared to be dirt which had been burnt but not removed. The globules appeared to be a result of dirt which had melted and fused to the stone. It was not clear whether these effects had damaged the stone but complete removal of the dirt required a fluence of 7 Jcm\(^{-2}\) at which it seems probable that conduction of heat into the stone would result in disruption and damage to the stone surface. Figure 2.34 shows an area (2.0 cm x 3.5 cm) of a lion's mask from Lincoln which has been cleaned by fixed-Q radiation. Most of the black crust (0.1 mm - 0.3 mm thick) has been removed leaving a surface with a similar texture and appearance to the clean areas of stone. Some powdery grey dirt remains.

Figure 2.34: Area of lion's mask cleaned by fixed-Q radiation. The irradiated area was given 3 pulses per 0.5 mm at 7 Jcm\(^{-2}\).

Figure 2.35, however, shows the effect of over-irradiating a fragile limestone surface in an attempt to remove the thin black crust completely. The surface has a rough texture and in some areas appears burnt.
Q-switched radiation was found to be at least an order of magnitude more efficient than fixed-Q radiation in the removal of black crusts; a fluence of only 0.5 J cm\(^{-2}\) was sufficient to remove the crust completely from the sculpture. Figure 2.36 shows an area (1.5 cm x 2.0 cm) which has been cleaned by Q-switched radiation; the limestone is left with a relatively smooth, light brown surface. The only remnants of dirt are left in areas which were 'missed' by the laser beam. At 0.5 J cm\(^{-2}\) three pulses were sufficient to clean an area 4 mm in diameter. Each pulse was accompanied by a cloud of material ejected from the crust, bright plasma formation and a loud 'snapping' sound. Upon irradiation of the cleaned area the plasma and acoustic pulse formation ceased. The surface of the stone appeared unaltered. However, by increasing the fluence sufficiently it was possible to remove material from the stone surface.

At a suitable fluence (determined by the properties of the crust and underlying stone) cleaning by Q-switched Nd:YAG radiation appears to be an efficient and selective process. Once the crust has been removed, further irradiation of the underlying stone appears to have very little effect. The laser beam interacts much more intensely with the black crust than the limestone. Due to the very short duration of the Q-switched pulse conduction of heat beneath the surface is not a problem.
Figure 2.36: Limestone sculpture cleaned by Q-switched radiation. Magnification x2.

Figure 2.37: Cleaned area of a limestone sculpture by Q-switched radiation.
Figure 2.37 shows the controlled cleaning possible with Q-switched radiation. A rough black pollution crust (between 0.1 mm and 0.5 mm thick) has been removed and the limestone left undamaged. The original tool marks can be seen running from the top to the bottom of the flower and the surface patina remains intact.

Effects on Sandstone

The effects of Q-switched Nd:YAG radiation on samples of the red and blonde sandstones described in section 2.3.4.2 have been briefly studied. The results are summarised in table 2.6.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Fluence / Jcm⁻²</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polluted red sandstone</td>
<td>1.0</td>
<td>1 pulse sufficient to remove polluted layers exposing a sandy brown surface.</td>
</tr>
<tr>
<td>Clean red sandstone</td>
<td>1.0</td>
<td>Surface grains lose their red colour. After 10 pulses surface has a white appearance. Individual grains appear undamaged.</td>
</tr>
<tr>
<td>Polluted blonde sandstone</td>
<td>1.0</td>
<td>1 pulse sufficient to remove crust. Surface composed of grey and colourless grains.</td>
</tr>
<tr>
<td>Clean blonde sandstone</td>
<td>1.0</td>
<td>10 pulses removed several grains leaving a small crater. Much of the white cement is removed giving the surface a light grey appearance.</td>
</tr>
</tbody>
</table>

Table 2.6: Summary of the effects of Q-switched radiation on polluted sandstone.

The results show that Q-switched radiation is able to remove polluted layers from the two types of sandstone studied. However, the process is not as selective as with limestone. Irradiation of the clean sandstone leads to modification of its surface. Interaction of Q-switched radiation with red sandstone appears to remove the red iron oxide coating from the silica grains. Interaction with blonde sandstone appears to
remove some of the white calcitic cement from between the grains. These results are similar to those obtained with dye laser radiation.

**Measurement of Absorption at 1.06 μm by Clean and Polluted Stone Surfaces**

The absorptivities of several stone surfaces at 1.06 μm have been measured without using an integrating sphere. Measurements were made by comparing the intensity of reflected radiation from the sample surface with the reflected intensity from a reference sample, as shown in figure 2.38.

![Figure 2.38: Measurement of absorption at 1.06 μm by comparison with a reference.](image)

Assuming that both the sample and standard are ideally diffuse reflecting surfaces, as discussed in section 2.3.3.2, then the proportion of incident radiation absorbed by the sample can be calculated using

\[ R_s = \frac{I_{\theta,s}}{I_{\theta,st}} R_* \]

where \( R_s \) and \( R_\ast \) are the reflectivities of the sample and standard respectively. \( I_{\theta,s} \) and \( I_{\theta,st} \) are the measured intensities of reflected radiation, at an angle \( \theta \), from the sample and standard respectively. The absorptivity, \( A_s \), can then be calculated from

\[ A_s = 1 - R_s \]

The distributions of reflected radiation from each sample surface were measured using a similar experimental arrangement to that shown in figure 2.19. A convex lens was used to focus the beam to a spot 4 mm in diameter on the surface of the sample, corresponding to a fluence of only 0.05 Jcm\(^{-2}\). When operated fixed-Q the fluence was
insufficient to modify the surface. A beam splitter was used to divert a portion of the incident beam to a Gentec calorimeter to monitor the energy of each pulse. The laser beam was incident at an angle of -20° to the surface normal. An integrating photodiode was used to measure the intensity of reflected radiation between +90° and -90° in steps of 10°. No measurements were made between 5° and 35° due to the experimental arrangement. Measurements were repeated between -90° and +90° and for each surface five areas were irradiated. For every surface a mean reflected intensity was calculated at each angle and plotted on a polar diagram. The photodiode was operated under reverse bias conditions as shown in figure 2.39.

![Photodiode Circuit Diagram](image)

**Figure 2.39: Circuit diagram for the operation of an integrating photodiode.**

The photodiode works in the following manner:

As light falls on the active area of the photodiode current flows. The external current $I$ is directly proportional to the incident light intensity. As the current flows a charge $q$ builds up on the capacitor $C$ where $q = VC$ but

$$q = \int I \, dt$$

so

$$V = \frac{1}{C} \int I \, dt$$

i.e. the voltage $V$ measured on an oscilloscope is proportional to the integral of the light intensity over the duration of the pulse.
The standard used in the experiment was a highly reflecting white tablet of co-dried aluminium hydroxide and magnesium carbonate which was assumed to have a reflectivity of 100%.

Each of the stone surfaces, clean and polluted, showed good agreement with the circular distribution of reflected radiation from an ideal diffuse reflecting surface. Typical distributions are shown in figures 2.40, 2.41 and 2.42.

![Diagram showing reflected radiation distribution](image)

**Figure 2.40:** Distribution of reflected radiation from the surface of the standard (assumed to have a reflectivity of 100%).

The relative reflectivity of a surface was calculated as the mean of the relative reflectivities at each angle between $-70^\circ$ and $+70^\circ$ for that surface. The calculated relative absorptivity at 1.06 $\mu$m for each surface is given in table 2.7.
Figure 2.41: Distribution of reflected radiation from a clean limestone surface (ball flower sculpture).

Figure 2.42: Distribution of reflected radiation from a polluted limestone surface (black crust on the ball flower sculpture).
Chapter 2: A Comparative Study of Laser Cleaning

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorptivity (±10%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clean surface</td>
<td>Polluted surface</td>
</tr>
<tr>
<td>Lincoln 1</td>
<td>10.30</td>
<td>20.92</td>
</tr>
<tr>
<td>Lincoln 2</td>
<td>10.20</td>
<td>30.89</td>
</tr>
<tr>
<td>Lincoln 3</td>
<td>10.28</td>
<td>30.88</td>
</tr>
<tr>
<td>Ancaster</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>White marble (unpolished)</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Blonde sandstone</td>
<td>0.44</td>
<td>0.86</td>
</tr>
<tr>
<td>Red sandstone</td>
<td>0.58</td>
<td>0.75</td>
</tr>
</tbody>
</table>

1 Limestone - broken interior surfaces.
2 Thin uniform black crust ~0.1 mm thick.
3 Dark grey crust 0.1-0.3 mm thick.

Table 2.7: Relative absorptivities of stone surfaces at 1.06 μm.

The results show that in general the absorptivity of a black crust is approximately a factor of 3 larger than the absorptivity of a clean limestone surface. Compared to the standard a typical crust absorbs between 75% and 90% of the incident radiation. The limestone samples absorbed between 20% and 30%. The sandstone samples absorbed a larger proportion of the incident radiation than the limestone. Hence, there exists a less significant difference between the absorptivities of clean and polluted sandstone surfaces. Marble absorbed only about 6% of the incident radiation. These results suggest that the selective removal of black crusts from limestone and marble surfaces should be possible. This has already been observed. It must be remembered, however, that the absorption properties of a stone surface or black crust can vary across that surface. In the case of one particular crust the relative absorptivity varied between 70% and 87%. Stone is an inhomogeneous substance and the values given in table 2.7 should be regarded only as a guide to the mean absorptivity of the surface as a whole. Comparisons between the relative absorptivities of clean and polluted surfaces can still be made.

2.3.4.5 Reflectivity Measurements Using a Spectrophotometer

The reflectivity of several polluted and clean stone samples has been measured using a U2000 double beam Hitachi spectrophotometer with an integrating sphere attachment. Measurements were carried out over the range 190-1100 nm. A typical reflectivity
spectrum is shown in figure 2.43. The reflectivity of each sample was measured at 248 nm, 590 nm and 1060 nm. Using these values the absorptivities were calculated. The results are summarised in table 2.8.

![Reflectivity Spectrum](image)

**Figure 2.43: Reflectivity spectrum for a black pollution crust on limestone.**

In general the results at 1060 nm agree with the measurements made in section 2.3.4.4: typical black crusts absorb between 80% and 95% of the incident radiation while clean stone surfaces absorb significantly less, particularly limestone (37%) and marble (26%). The absorptivities of the limestone and Huskisson marble samples measured by the spectrophotometer are slightly higher than those measured in section 2.3.4.4. It should be remembered that: (i) the values measured in the previous section are only relative to the standard used and have been based on the assumption that each sample is an ideal diffuse reflecting substance and (ii) different samples have been used (including a different type of marble).

At each wavelength (248 nm, 590 nm and 1060 nm) polluted surfaces absorbed more energy than clean surfaces, with the difference being least significant for red and blonde sandstone. The polluted surfaces absorbed a larger proportion of incident radiation at 590 nm and 1060 nm than at 248 nm. An important result was obtained for the patinated marble surface: only about 32% was absorbed at 1060 nm, compared to 62% at 590 nm and 80% at 248 nm. If a sculpture is to be cleaned without damage to the patina of the stone then it is important that most of the radiation is reflected from the surface. This appears to be the case with Nd:YAG radiation.
Chapter 2: A Comparative Study of Laser Cleaning

<table>
<thead>
<tr>
<th>Stone</th>
<th>Clean/Polluted</th>
<th>Absorptivity / (± 10%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>248 nm</td>
<td>590 nm</td>
<td>1060 nm</td>
<td></td>
</tr>
<tr>
<td>Red sandstone</td>
<td>Clean</td>
<td>0.53</td>
<td>0.73</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polluted</td>
<td>0.75</td>
<td>0.88</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Blonde sandstone</td>
<td>Clean</td>
<td>0.62</td>
<td>0.65</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polluted</td>
<td>0.76</td>
<td>0.90</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Lincoln limestone</td>
<td>Clean</td>
<td>0.29</td>
<td>0.46</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polluted</td>
<td>0.75</td>
<td>0.90</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Huskisson marble</td>
<td>Clean</td>
<td>0.19</td>
<td>0.19</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Patina</td>
<td>0.80</td>
<td>0.62</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polluted</td>
<td>0.85</td>
<td>0.95</td>
<td>0.93</td>
<td></td>
</tr>
</tbody>
</table>

1 Broken surface.

2 Thick (0.1-1.0 mm) hard black crust.

3 White marble with crumbling 'sugary' surface.

4 Smooth soft black pollution layer ~ 0.1 mm thick.

Table 2.8: Summary of absorptivity measurements made using a spectrophotometer.

2.3.5 Summary

The interactions of four types of laser radiation (extending from the ultraviolet to the infrared) with polluted and clean stone sculpture have been qualitatively studied. This work has shown that a Q-switched Nd:YAG laser is the most suitable laser for the removal of black crusts from limestone and marble sculpture. The absorptivity of typical polluted layers is between 2.5 and 3.5 times higher than the absorptivity of a typical limestone or marble surface. This large difference is an important factor in the selective removal of polluted layers. The pulse length of laser radiation is also an important factor; fixed-Q Nd:YAG radiation (100 µs) has been shown to be less efficient in removing polluted layers, as heat is conducted away from the surface region throughout the duration of the pulse; a pulse of several nanoseconds is too short for heat to be conducted into the body of the stone.
Cleaning tests have been carried out in which hard, black crusts have been completely removed from fragile limestone sculpture without damaging the underlying stone. The Glasgow sandstones which have been tested were found to be more strongly absorbing than the limestones. Consequently cleaning was not as selective and at higher fluences it was possible to modify the appearance of the stones by removing surface material. The Nd:YAG laser is also the most practical laser for cleaning sculpture; such lasers are usually of rugged construction, can be operated for long periods of time at repetition rates of up to 30 Hz and involve no contact with hazardous chemicals.
References


CHAPTER 3

INTERACTION OF LASER RADIATION WITH STONE

3.1 Introduction

This chapter describes the interaction of laser radiation with stone surfaces. Two techniques have been developed which demonstrate the self-limiting nature of Nd:YAG laser radiation in the cleaning of stone sculpture:

(i) Threshold laser fluences for the removal of material from clean and polluted stone have been measured by the detection of light scattered as a result of interaction with particles which have been ejected from the surface.

(ii) Measurement of the amplitude of the acoustic pulse generated during the interaction of laser radiation with stone has been used to monitor the cleaning process.

These techniques are described and results presented for samples of limestone, sandstone and marble. Initial experiments have also been carried out using a transducer to monitor the longitudinal wave generated within a thin stone sample during removal of material from the surface.

3.2 Effects Due to Absorption of Laser Radiation

When a laser beam is incident on a solid sample some of the energy is absorbed by various mechanisms, depending on the nature of the sample and the wavelength of the radiation, while the rest is either reflected or scattered. At low incident powers absorption can lead to the generation of thermal waves, elastic waves and in semiconductors electric currents may be caused to flow. At higher powers material may be ablated from the surface, as has been observed in chapter two, while in the sample there may be melting, plastic deformation and formation of cracks [1].
3.2.1 Ablation

In a metal electromagnetic radiation interacts with the surface, causing electric currents to flow in the conduction band electrons. Some of the energy is absorbed by resistive losses, such as electron-phonon scattering, while the rest is reflected. The interior of the metal is screened from the radiation by the conduction electrons at the surface so that absorption and reflection occurs within a surface layer or 'skin'. The skin depth is defined as the depth at which the amplitude of the electromagnetic wave falls to e⁻¹ of its initial value. In a metal the skin depth is typically of the order of nanometres and depends on the wavelength of the incident radiation and the electrical conductivity and permeability of the metal. For aluminium, at 1.06 μm, the skin depth is approximately 5 nm. In a non-metal the radiation penetrates further into the sample, to a depth of the order of microns. Absorption of radiation can lead to ablation (the ejection of material from the surface of a sample as a result of intense laser irradiation) by different processes, depending on the wavelength of the incoming radiation. This has been observed with organic polymers [2,3]:

(i) Photochemical process; The absorption of ultraviolet radiation by a molecule can involve an electronic transition to a higher state. This might simply lead to the conversion of energy into heat and no reaction but if the transition leads to a level above the dissociation limit then the molecule can dissociate. The products have a larger specific volume than the original sample and an explosion occurs. Photochemical ablation occurs as long as the excitation is greater than about 3.6 eV (λ < 340 nm).

(ii) Thermal process; For irradiation at wavelengths corresponding to energies less than the chemical bond strengths (λ > 340 nm) one photon is not sufficiently energetic to force a molecule to undergo an electronic transition such that a bond is broken. Consequently, the energy is absorbed into the vibrational modes of the molecule, either directly or indirectly via a low-lying electronic state. This is essentially a heating process. Eventually one bond may absorb a sufficient number of photons to initiate dissociation. Ablation of material then corresponds to evaporation rather than a volume explosion.

In chapter two it was established that a Nd:YAG laser is the most suitable type of laser for cleaning stone sculpture. Such a laser emits in the near infrared so the process of thermal ablation is dominant. Since the absorbed energy mostly takes the form of heat, laser irradiation induces a temperature rise at the surface and in the case of an
insulator, in the bulk of the sample also. Thermal conductivity ensures that the heat eventually becomes distributed throughout the sample. The temperature distribution resulting from absorption of a laser pulse can be calculated from the differential equation for heat flow in a semi-infinite slab with a boundary plane at $z = 0$ [4]:

\[
\frac{\partial^2 T(z,t)}{\partial z^2} + \frac{1}{k} \frac{\partial T}{\partial t} = \frac{-A(z,t)}{K}
\]

where $T(z,t)$ is the temperature distribution, $A(z,t)$ is the heat production per unit volume per unit time, $K$ is the thermal conductivity and $k$ is the thermal diffusivity. The following assumptions have been made:

(i) There is no phase change.
(ii) The thermal properties of the material are independent of temperature.
(iii) A local thermal equilibrium is established during the pulse.
(iv) Negligible energy is lost from the surface by radiation.
(v) The absorbed laser flux is uniform across the irradiated area.

The differential equation has been solved [5] to give the approximate temperature rise at the surface of a sample as

\[
T(t) = \frac{2 \alpha I}{K} \frac{\sqrt{kt}}{\pi}
\]

where $\alpha$ is absorptivity and $I$ is laser beam power density. This result is valid for the duration of the pulse, $t_0$. For $t > t_0$, a second term must be added to represent switching off. At the surface the temperature rises for the duration of the pulse (while energy is still being absorbed) to a maximum. Once the laser pulse finishes the temperature falls as heat is conducted into the bulk. The maximum temperature rise at increasing depth below the surface is less and occurs later. For aluminium, irradiated by a 20 ns laser pulse with $\alpha I = 2 \times 10^{10}$ Wm$^{-2}$, maximum temperature rises of 130 °C at the surface and 40 °C at 2 μm below the surface have been calculated [1]. In a non-metal the temperature decays exponentially from a maximum at the surface, while the time-dependence of the temperature is the same as the energy in the pulse. For polluted stone, assuming the black crust to be composed purely of carbon and the underlying
Chapter 3: Interaction of Laser Radiation With Stone

stone purely of calcite (having the properties shown in Table 3.1), irradiation by a 20 ns pulse at a fluence of 0.1 J cm\(^{-2}\) would induce a maximum temperature rise at the polluted surface of 3700 °C and at the stone surface of only 750 °C [6]. The carbon layer would, therefore, be vaporised but the underlying stone surface would remain at a temperature below 899 °C, above which calcite decomposes. These calculations should only be treated as an approximate guide to the temperature increases induced by absorption of a laser beam as black crusts and stone are inhomogeneous substances and cannot be treated as simply as they have been here. However, these results do show that absorption of a laser beam leads to a much larger temperature increase in the surface of a strongly absorbing black crust than in the surface of a weakly absorbing limestone. At suitable fluence selective vaporisation of the black crust should, therefore, be possible. These calculations support the observations already made and discussed in chapter two.

<table>
<thead>
<tr>
<th>Property</th>
<th>Black Crust</th>
<th>Limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorptivity, (\alpha)</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Thermal conductivity, (K) /Wm(^{-1})k(^{-1})</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Thermal diffusivity, (k) /m(^2)s(^{-1})</td>
<td>(1.06 \times 10^{-6})</td>
<td>(2.04 \times 10^{-6})</td>
</tr>
</tbody>
</table>

Values from 'Tables of Physical and Chemical Constants', Kaye and Laby. Values are approximate and should be regarded as typical values only.

Table 3.1: Properties of a 'typical' black crust and limestone used in calculations of the maximum surface temperature rise resulting from absorption of a laser pulse.

If the black crust and limestone surfaces are irradiated under the same conditions but with the laser operated fixed-Q, so that the pulse length is about 100 \(\mu\)s the corresponding maximum temperature rises at the surfaces are only 52 °C and 10 °C respectively. These small temperature increases for fixed-Q pulses are due to the relatively long duration of the laser pulse; as energy is deposited during the pulse, heat is conducted away from the surface into the bulk. A Q-switched laser pulse deposits heat energy so quickly that very little is conducted away. Thermal diffusion lengths of 28 \(\mu\)m and 0.4 \(\mu\)m for a limestone sample irradiated by fixed-Q and Q-switched radiation respectively have been calculated.
As has already been mentioned, irradiation of a surface at high power densities can lead to the vaporisation of material. The mechanism by which this occurs depends on the duration of the laser pulse, i.e. whether the pulse is Q-switched or of microsecond duration [4]:

- When an ordinary laser pulse (microsecond duration) is used to vaporise material the temperature of the surface is raised to its vaporisation temperature in a time short compared to the pulse duration. This is true even if the surface is initially quite reflecting. At high temperatures, when vaporisation begins, the radiation is absorbed very efficiently with little reflection. Absorption then occurs at a continually retreating vaporising surface, with constant removal of the vaporised material. The duration of the pulse is sufficiently long for the vaporised material to leave the surface and move away. Some of the material removed emerges as unvaporised globules which are carried away from the surface by a small amount of vaporised material. There is little absorption in the plume of vaporised material.

- For a Q-switched laser pulse heat absorption occurs too rapidly for vaporisation to proceed as with an ordinary laser pulse. The surface of the material rises to its vaporisation temperature and begins to vaporise. The material recoiling against the surface produces a high pressure pulse. This pressure pulse raises the boiling point of the underlying material which becomes superheated as more energy is absorbed. Eventually, as the temperature rises high enough the heat of vaporisation falls to zero. At this point there is no distinction between the superheated solid and a highly condensed gas and the emission of material proceeds like a thermal explosion. Unlike an ordinary laser pulse the plume of vaporised material is not transparent. The material in the plume is at a high temperature and there is considerable thermal ionisation.

### 3.2.2 Plasma Formation

Irradiation of a surface at sufficiently high power densities leads to the vaporisation of material. Absorption of a fraction of the energy contained in the incoming laser pulse gives rise to intense heating and ionisation of the ejected material which forms a spark or plasma. The formation of a plasma in the vicinity of the surface dominates the later transfer of energy and momentum to the solid.
As the plasma absorbs energy from the laser pulse, it becomes extremely hot. At a sufficiently high density (critical particle density $\sim 10^{21}$ cm$^{-3}$) the plasma acts as a shield; radiative transport of laser energy is cut off and heat conduction by electrons becomes the principal mechanism of energy transport through the overdense plasma to the sample [7]. The incident laser energy is strongly absorbed in a thin layer of the plasma, resulting in rapid heating and expansion which produces an impulse reaction on the surface. The temperature of the plasma is determined by the rate of energy increase due to laser heating and the rate of energy loss due to plasma expansion. The plasma expands adiabatically, with the absorbing plasma layer at the critical density propagating towards the laser. Most of the thermal energy of the plasma is in the form of kinetic expansion energy of the ions. The surface impulse produced by vaporisation of material and subsequent plasma expansion (shown schematically in figure 3.1) is dominated by the fast-moving ionised component of the ejected material.

![Diagram showing the interaction of laser radiation with stone](image)

**Figure 3.1:** Schematic diagram showing the net reactive force due to ablation of surface material and plasma formation.

Measurements made during the interaction of a 300 MW, 20 ns Nd:YAG laser pulse with a thick aluminium target showed that 10% of the total ejected mass appears in ionised form and that the ionised particles account for 80% of the total momentum transferred to the target [7]. A study of the interaction of a 30 MW Q-switched laser pulse with a carbon block [8] revealed that the plasma does not appear until a few nanoseconds after the laser pulse has reached its peak value and that the plasma is still present, although diminished in brightness, almost a microsecond after the laser pulse.
3.2.3 Thermoelastic Stresses

In the low power regime the only effect of the incident laser pulse is a modest increase in temperature of the surface region of the sample, which is accompanied by thermal expansion of the heated material and subsequent generation of stresses and strains within the sample [1]. The thermoelastic stresses generate elastic waves (*ultrasound*) which propagate deep within the sample. This is illustrated schematically in figure 3.2.

![Thermal wave field](image)

**Figure 3.2:** Schematic representation of the generation of elastic waves within a solid due to absorption of laser radiation.

The source of elastic waves can be considered equivalent to the insertion of a small extra volume of material dV at the irradiated region, where dV can be approximated using [1]

\[
\text{dV} = \frac{3\alpha}{\rho C} \text{dE}
\]

where \(\alpha\) is the coefficient of linear thermal expansion, \(\rho\) is the density, \(C\) is the specific heat capacity and dE is the energy absorbed from the laser pulse. For an aluminium sample, absorption of 1 mJ of energy uniformly over an area 10 mm\(^2\) yields a value of \(\text{dV} = 3 \times 10^{-14}\) m\(^3\). Assuming that the source has a thickness of 2 \(\mu\)m, which is the depth within which most of the temperature rise occurs in aluminium, the generated thermoelastic stresses are of the order of \(10^8\) PamJ\(^{-1}\) absorbed energy [1]. In aluminium the yield stress is of the same order. It is, thus, relatively easy to exceed the yield stress locally and cause permanent damage if too high a power density is used.
These stresses are of the same order of magnitude as those due to ablation at higher power densities. The reason that the thermoelastic stresses are so high is that a Q-switched laser pulse deposits heat energy so quickly that very little is conducted away, so that a substantial temperature rise is contained within a small volume, generating high compressive stresses due to expansion of the material.

3.2.4 Other Effects

3.2.4.1 Radiation Pressure

Electromagnetic radiation incident on a solid surface generates a pressure due to the change in momentum of the photons as they are reflected or absorbed at the surface. The magnitude of the radiation pressure, $P$, can be calculated \[1\] from

$$P = \frac{(1+R)I}{c}$$

where $I$ is the power density of the incident wave, $R$ is the reflectivity of the surface and $c$ is the velocity of light. For a pulse of incident energy $dE$, duration $dt$, uniformly illuminating an area $A$, the average radiation pressure during the pulse is

$$P = \frac{(1+R)dE}{cA dt}$$

By way of example, a 20 ns, 100 mJ laser pulse incident over an area 10 mm$^2$ will generate a radiation pressure of approximately 2800 Pa for a reflectivity of 0.7. The mean force experienced normal to the surface during the pulse is, thus, 0.028 N. The forces and stresses on a solid resulting from radiation pressure are generally several orders of magnitude less than those due to thermoelastic effects and ablation. For the purpose of laser cleaning, radiation pressure can therefore be considered negligible.

3.2.4.2 Acoustic Pulse Formation

At low pulse energies absorption of laser radiation at a surface leads to heating of the air immediately above the surface. If the laser pulse is Q-switched then rapid
expansions of the heated surface region of the sample and the air above it together lead to the creation of an acoustic pulse which propagates away from the surface. At higher power densities, when some material is vaporised and solid particles are ejected from the surface (with a velocity of the order of $10^4$ cms$^{-1}$ [9]), compression and rarefaction of the air in the vicinity of the interaction leads to the creation of a shock pulse which is audible as a 'snapping' sound. At sufficiently high power densities, when a plasma is formed, rapid expansion of the plasma gives rise to an increased amplitude shock pulse which expands hemispherically from its source at the surface. The loudness of the shock pulse is dependent on the strength of the interaction between the laser pulse and surface.

### 3.3 Mechanisms of Laser Cleaning

As has been seen in section 3.2 the interaction of a Q-switched laser pulse with a solid surface is a complex process. Four mechanisms contribute to the removal of black crusts from stone sculpture by Q-switched Nd:YAG laser radiation. The relative importance of each mechanism is dependent on the energy of the laser pulse. These mechanisms are:

(i) *Thermal expansion,* absorption of energy within a small, well-defined volume can lead to the generation of thermoelastic stresses which are sufficient to break bonds within the crust. Additional energy absorbed from the pulse is used as kinetic energy in ejection of the solid particles from the surface.

(ii) *Explosive vaporisation,* at sufficiently high power densities vaporisation of surface material occurs. Initially, the surface of the crust is raised to a temperature above its vaporisation temperature and begins to vaporise. The material recoiling against the surface induces a pressure pulse in the crust which raises the boiling point of the underlying material. The emission of further vaporised material then proceeds like a thermal explosion, as described in section 3.2.1.

(iii) *Surface relaxation,* at high power densities, rapid expansion of the plasma formed by initial vaporisation of material applies an impulse reaction to the irradiated region of the crust. Once the laser pulse has finished, relaxation of the surface leads to the further ejection of material from the crust.
(iv) *Shock-induced surface disruption;* at high power densities, propagation of the acoustic shock pulse along the surface of the crust generates stresses which are sufficient to cause physical disruption to material in the vicinity of the irradiated region.

Each of these mechanisms contributes to the cleaning process. At low power densities, when the temperature rise induced in the crust is insufficient to cause vaporisation and subsequent plasma formation, the process of *thermal expansion* is responsible for the removal of material from the crust. At high power densities the processes of *explosive vaporisation, surface relaxation* and *shock-induced disruption* become dominant.

### 3.4 Threshold Fluence Measurements for the Removal of Polluted Layers from Stone Sculpture.

Detection of light scattered by material ejected from a stone surface has been used to determine threshold fluences for the removal of material from polluted and clean stone by both Q-switched and fixed-Q Nd:YAG laser radiation. Measurements have been made for samples of polluted limestone, sandstone and marble.

#### 3.4.1 Introduction

Helium-neon laser beam deflection, or *photothermal deflection*, has previously been used to study excimer laser ablation of polymers and a superconductor [10, 11]. The technique involves passing a HeNe probe beam parallel to the substrate surface, but displaced from it by typically a few hundred micrometres to a few millimetres. A position-sensitive detector, located about 25 cm away, measures the deflection angle of the probe beam due to the refractive index gradients in the gas above the sample from the pulsed ultraviolet laser incident normally to it. This technique has provided information about threshold fluences and ablation product velocity.

*Schlieren* photography has previously been used to show the evolution of shock waves, sound waves and hot gas plumes resulting from excimer laser ablation of polymers [12]. In this technique, the probe beam (a pulsed rather than continuous laser beam) is brought to a focus on a circular stop or knife edge. Any deflection of the probe beam resulting from interaction of the ultraviolet laser beam with the substrate.
deflects light past the filter [13], giving rise to an intensity change on the photographic film.

The technique which has been developed to measure threshold fluences for removal of material from stone surfaces is based on the photothermal deflection and schlieren techniques outlined above. The principal is shown in figure 3.3. A collimated HeNe probe beam is passed parallel to the stone sample so that it grazes the surface. The beam is brought to a focus on a circular stop so that no light reaches the CCD camera. The Nd:YAG laser beam is incident normal to the sample surface. When the fluence exceeds the threshold value, material is ejected from the surface and light from the probe beam is deflected past the schlieren stop and imaged onto the CCD camera. The ejection of material from the stone surface can, therefore, be viewed on the monitor as a sudden increase in light intensity.

![Diagram of threshold fluence measurement](image)

**Fig 3.3:** Schematic representation of threshold fluence measurements by scattering of light from a probe beam.

Above threshold, light is deflected past the stop in three ways:

(i) **Diffraction:** light is diffracted past the stop by particles ejected from the stone surface which are of a similar size to the wavelength of the probe beam. For a HeNe beam (632.8 nm) diffraction occurs with 0.1 μm size particles.
(ii) **Refraction;** light is bent as a result of refractive index gradients in the gas above the surface of the stone. These arise from the vaporisation of surface material and the formation of a hot, dense, plasma.

(iii) **Scattering;** as light from the probe beam interacts with particles ejected from the stone surface it is reflected, or scattered, in many directions. Some light is scattered towards the camera and deflected past the stop.

At fluences well above threshold, the ejection of material from the stone is viewed on the monitor as a series of fast-moving bright specks of light superimposed on a uniformly illuminated background, with bright rings appearing around some of the specks. The background is due to deflection by plasma formation and the rings are due to diffraction effects. At fluences close to threshold only the fast-moving specks of light are seen. The arrangement used was not sensitive enough to detect deflections of the probe beam due to heating of gases above the sample surface, at fluences below threshold.

### 3.4.2 Experimental Procedure

The experimental arrangement is shown schematically in figure 3.4. A 10 mW collimated HeNe laser beam was passed through a spatial filter and expanded to 10 mm diameter. The beam passed parallel to the stone sample, grazing the surface, and was brought to a focus (spot size 1.5 mm diameter) in the centre of a 3 mm diameter schlieren stop. The Nd:YAG laser beam was brought to a focus several millimetres before the stone surface so that the beam impact spot was 5 mm diameter. With the laser operating Q-switched (20 ns pulses) it was necessary to use attenuators to reduce the beam energy sufficiently. It was not possible to monitor the energy of each pulse by reflection from a glass slide because of the low sensitivity of the calorimeter. The output energy of the laser was measured using a Gentec calorimeter prior to the experiment. The energy per pulse was found to be constant to ±5%.

Due to lens aberrations and scattering of the probe beam from the stone surface, a small portion of the beam always reached the camera. The ejection of material from a sample was viewed as a change in the light intensity pattern on the monitor. During the course of the experiment the number of attenuators and spot size were kept constant. The fluence\(^1\) was varied by adjusting the voltages on the oscillator and amplifier. At

\[^1\text{Fluence is average fluence unless otherwise stated, i.e. total energy per pulse/spot size.}\]

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each fluence five areas of the sample surface were tested. The fluence was then gradually increased and the process repeated until the threshold fluence had been reached. Samples of Lincoln and Ancaster limestone, white marble and blonde and red Glasgow sandstones were tested. The experiment was repeated for fixed-Q radiation.

Figure 3.4: A schematic representation of the experimental arrangement used for threshold fluence measurements.

### 3.4.3 Results

The results are given as probabilities\(^2\) of material removal at each fluence because of the inhomogeneous nature of black crusts and stone surfaces. Instead of giving a single threshold fluence for each surface, two values are given. The first is the maximum fluence at which the probability of material removal is 0%, i.e. no material is removed irrespective of the number of pulses fired. The second is the minimum fluence at which the probability of material removal is 100%, i.e. at and above this fluence material is removed from the surface with each pulse fired.

The results for Q-switched radiation are summarised in table 3.2.

---

\(^2\)In this context the term *probability* is used to describe the *proportion* of tests in which material was ejected from the stone surface.
Table 3.2: Summary of fluences measured at 0% and 100% probabilities of material removal by Q-switched pulses.

The results for Lincoln limestone and red sandstone are presented in graphical form in figure 3.5.

![Figure 3.5: Probability of material removal from stone surfaces as a function of fluence.](image)

The results show that material is removed from the polluted layers at lower fluences than from the clean stone surfaces (limestone, sandstone and marble). In general,
ejection of material from a black crust occurs at a fluence approximately half that for a clean surface at 100% probability (13 mJcm\(^{-2}\) compared to 25 mJcm\(^{-2}\)). The corresponding results for material removal from clean surfaces by fixed-Q radiation are summarised in table 3.3.

<table>
<thead>
<tr>
<th>Stone</th>
<th>Surface</th>
<th>Fluence Jcm(^{-2}) (+20%)</th>
<th>Probability = 0%</th>
<th>Probability = 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lincoln limestone</td>
<td>Clean broken</td>
<td>0.11</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Ancaster limestone</td>
<td>Clean</td>
<td>0.06</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>White marble</td>
<td>Clean</td>
<td>0.13</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Red sandstone</td>
<td>Clean</td>
<td>0.16</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Blonde sandstone</td>
<td>Clean</td>
<td>0.08</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Summary of fluences measured at 0% and 100% probabilities of material removal by fixed-Q pulses.

These results show that removal of material from stone surfaces by fixed-Q, relatively long duration pulses, requires a higher fluence than by Q-switched pulses. The results in table 3.3 are almost one order of magnitude larger than the corresponding results for Q-switched pulses.

3.4.4 Conclusions

This technique has shown to be sensitive enough to detect the ejection of very small amounts of material from a stone surface, without the formation of a plasma. It is, thus, capable of detecting events which are not visible to the unaided eye. At low fluences (~20 mJcm\(^{-2}\)) removal of material by Q-switched pulses was viewed on the monitor as fast-moving specks of light with occasional diffraction effects. This suggests that small particles were ejected from the stone surface as a result of rapid thermal expansion of the heated region. There appeared to be no vaporisation.

The results have shown that pulsed Nd:YAG laser radiation is more efficient in removing material from black pollution crusts than from clean limestone, sandstone and marble surfaces. The threshold fluences for material removal by Q-switched pulses are typically [0.012, 0.025] Jcm\(^{-2}\) for clean surfaces and [0.003, 0.013] Jcm\(^{-2}\) for polluted surfaces. The results are presented as [x, y], where x is the 0% probability and y the 100% probability. In general, at 100% probability the threshold fluence for a
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polluted surface is approximately half that for a clean stone surface. This shows that selective removal of a black crust from a stone surface is possible. However, at such low fluence very little material is removed from the crust and for cleaning purposes a fluence of 0.1 Jcm\(^{-2}\) is more reasonable. Care must, therefore, be taken not to damage the underlying stone. Irradiation of a clean surface at 0.1 Jcm\(^{-2}\) might lead to the ejection of a small number of loosely bound particles as a result of thermal expansion of the heated region.

The results also showed that, as expected, threshold fluences for removal of material by fixed-Q pulses are almost one order of magnitude higher than those for Q-switched pulses. Typical values of [0.1, 0.2] Jcm\(^{-2}\) for limestone were measured. This is a consequence of the relatively long pulse duration; as energy is absorbed at the surface heat is also being conducted into the bulk of the sample.

3.5 Acoustic Monitoring of the Interaction of Laser Radiation with Stone

As described in section 3.2, the rapid ejection of material from a stone surface leads to the creation of a shock pulse in gases close to the interaction which is audible as a 'snapping' sound. The amplitude of this shock pulse has been monitored during cleaning to evaluate the strength of the interaction of a Q-switched laser pulse with polluted and clean stone surfaces.

3.5.1 Introduction

The formation of acoustic waves in air as a result of laser ablation of materials has been discussed in a number of papers [11, 14-16]. Research has shown [16] that at incident laser fluences below the ablation threshold, the acoustic signal is produced by the thermal expansion of air near the irradiated surface (thermal-piston signal). Above the ablation threshold the acoustic signal contains an additional component due to the ejection of ablated materials (ablative-piston signal). The amplitude of the ablative-piston signal has been found to be a monotonic function of the etch-depth per pulse. Schlieren study of the acoustic pulse generated by excimer laser ablation of a polymer [11] indicated a transition from a sound wave below the ablation threshold to a shock wave above threshold.
To monitor the interaction of a Q-switched Nd:YAG laser pulse with polluted stone surfaces a simple dynamic coil microphone, with a frequency response of 100 Hz to 12 kHz, has been used to detect the acoustic pulse generated in the gases above the irradiated area. The output from the microphone was displayed on a storage oscilloscope in the form of a voltage pulse with a time period of 400 µs. The amplitude of this voltage pulse is assumed to be proportional to the 'strength of the interaction' of the laser pulse with the stone surface. Using a microphone and an experimental arrangement similar to that shown in figure 3.4, the intensity of scattered light has been measured as a function of the acoustic pulse amplitude [17] for irradiation of a polluted limestone surface at 0.8 Jcm⁻². The results have been plotted in figure 3.6.

![Figure 3.6: Relationship between intensity of scattered light and acoustic pulse amplitude.](image)

The results show that there exists a strong linear relationship between the intensity of light scattered by ejected particles and the amplitude of the acoustic pulse generated as a result of the interaction. Assuming the intensity of scattered light to be proportional to the quantity of material removed from the surface, then the amplitude of the acoustic pulse is also dependent on the quantity of ejected material, i.e. as the interaction of the laser pulse with the surface becomes more intense, more material is ablated and the acoustic pulse becomes louder. From figure 3.6 it can be seen that the line of best fit does not pass through the origin. This is probably due to the fact that although there is no ablation an acoustic pulse is still produced by thermal expansion of
the air near the irradiated surface. Similar results have been obtained at a fluence of 0.4 \( \text{Jcm}^{-2} \).

### 3.5.2 Experimental Procedure

A schematic representation of the experimental arrangement is shown in figure 3.7.

![Diagram of experimental arrangement](image)

Figure 3.7: Schematic representation of the experimental arrangement used for acoustic monitoring of the cleaning of stone.

The acoustic pulse amplitude has been measured as a function of the number of laser pulses for three polluted stone surfaces: (i) Lincoln limestone, (ii) a light brown sandstone from Lincoln and (iii) red Glasgow sandstone. In each case the angle of the microphone to the surface normal and its distance from the surface were kept constant [17]. The black crusts were irradiated at a fluence exceeding the ablation threshold. The experiment was repeated five times with each sample and the results averaged.

### 3.5.3 Results

#### 3.5.3.1 Lincoln Limestone

The polluted limestone surface was irradiated by Q-switched pulses at 0.8 \( \text{Jcm}^{-2} \) until the crust had been completely removed. A clean surface was also irradiated. The averaged results are shown in figure 3.8.
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Figure 3.8: Acoustic pulse amplitude as a function of number of pulses for clean and polluted limestone surfaces.

Figures 3.9 and 3.10 show the state of the surface prior to irradiation and after ten pulses respectively.

Figure 3.9: Black crust prior to irradiation. (Magnification x11).

Figure 3.10: Surface after 10 pulses. (Magnification x11).
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The acoustic pulse amplitude is initially at a maximum. As the number of pulses increases, the amplitude decreases rapidly, until after approximately ten pulses when it levels off at the value for the clean surface. The decrease in acoustic pulse amplitude corresponds to the cleaning of the stone surface. Initially, the laser pulse interacts strongly with the black crust and material is ablated. As the crust is removed and the underlying limestone gradually exposed, the interaction of each pulse with the surface becomes weaker and less material is ablated. Finally, after 10 pulses the crust has been completely removed and further pulses interact only very weakly with the limestone. Further irradiation of the clean limestone at 0.8 J cm⁻² gives rise to a very small amplitude acoustic pulse, approximately 1% of the initial acoustic pulse generated by interaction with the black crust. This is due, in part, to expansion of the air above the heated surface region. These results are typical for the removal of black crusts from polluted limestone.

3.5.3.2 Lincoln Sandstone

The acoustic pulse amplitude has been measured as a function of the number of laser pulses for a polluted sandstone surface. Removal of the black crust has been achieved by: (i) Q-switched pulses at 1 J cm⁻² and (ii) fixed-Q pulses at 7 J cm⁻². The results are shown in figures 3.11 and 3.12.

In general the graphs have a similar shape to that obtained for polluted limestone. As the black crust is removed the interaction of the laser pulse with the stone surface becomes weaker and less material is ablated. Figure 3.11 shows an initial increase in the acoustic pulse amplitude. This corresponds to a darkening of the surface as surface material is removed and an underlying carbon layer exposed.

Figures 3.13 - 3.15 show the state of the surface prior to irradiation, after 1 and after 50 Q-switched pulses at 1 J cm⁻² respectively. After 1 pulse the crust has darkened and after 50 pulses the crust has been completely removed exposing the individual grains of silica. Figures 3.16 - 3.18 show the corresponding photographs for irradiation by fixed-Q pulses at 7 J cm⁻². After 1 pulse the crust has been partially removed. After 50 pulses the crust has been completely removed, but the underlying silica grains appear to have suffered damage due to thermal effects.
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Figure 3.11: Acoustic pulse amplitude as a function of number of Q-switched pulses at 1 Jcm⁻².

Figure 3.12: Acoustic pulse amplitude as a function of number of fixed-Q pulses at 7 Jcm⁻².
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Figure 3.13: Black crust prior to irradiation. (Magnification x20).

Figure 3.14: Black crust after 1 Q-switched pulse at 1 Jcm\(^{-2}\).

Figure 3.15: Sandstone surface after 50 Q-switched pulses at 1 Jcm\(^{-2}\).

Figure 3.16: Black crust prior to irradiation. (Magnification x20).

Figure 3.17: Surface after 1 fixed-Q pulse at 7 Jcm\(^{-2}\).

Figure 3.18: Sandstone surface after 50 fixed-Q pulses at 7 Jcm\(^{-2}\).
3.5.3.3 Red Glasgow Sandstone

The acoustic pulse amplitude has been measured as a function of the number of laser pulses for clean and polluted surfaces of the red Glasgow sandstone described in section 2.3.4.2. The surfaces were irradiated by Q-switched pulses at a fluence of 0.33 Jcm⁻². The results have been plotted in figure 3.19.

![Acoustic Pulse Amplitude vs. Pulse Number](image)

Figure 3.19: Acoustic pulse amplitude as a function of number of Q-switched laser pulses for red sandstone.

The curve for the polluted surface is a similar shape to the curve for a polluted limestone surface; the amplitude decreases rapidly as the crust is removed and the underlying stone exposed. However, the curve for the clean surface is more pronounced than for clean limestone indicating that there is a stronger interaction with the clean sandstone surface. In fact, after 2 pulses the curves for irradiation of the clean and polluted sandstone are, within the error bars, identical. Between 2 and 10 pulses the curves decrease rapidly as material is ejected. Since the black crust has been completely removed after 2 pulses, this further decrease in acoustic pulse amplitude is due to removal of the red iron oxide coating from the silica grains. After 10 pulses the curves level off, once the pigment has been completely removed, exposing the underlying silica grains. This can be clearly seen in figures 3.20-3.25.
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Figure 3.20: Black crust. (Magnification x6).

Figure 3.23: Clean surface. (Magnification x6).

Figure 3.21: Polluted surface after 2 pulses. Crust has been completely removed from irradiated region.

Figure 3.24: Clean surface after 2 pulses. Pigment has been partially removed from irradiated region.

Figure 3.22: Polluted surface after 10 pulses. Pigment has been removed from central grains in irradiated region.

Figure 3.25: Clean surface after 10 pulses. Pigment has been removed from irradiated grains.
3.5.4 Conclusions

Monitoring of the acoustic pulse generated by ablation of material from a stone surface is a useful non-contact technique in the characterisation of the removal of black crusts by laser radiation. The acoustic pulse amplitude is proportional to the intensity of the interaction of the laser pulse with the irradiated surface and can be used as an approximate measure of the quantity of material ablated. Results have been presented which clearly demonstrate the selective removal of polluted layers from limestone sculpture. A Q-switched Nd:YAG laser pulse interacts strongly with a black crust resulting in ablation of surface material and the subsequent generation of a large amplitude acoustic pulse. As the crust is removed and the underlying limestone exposed, further laser pulses result in a decrease of the amplitude as less material is ablated. Once the crust has been completely removed the amplitude falls to approximately 1% of its initial value due to the weak interaction of the laser pulse with the limestone surface. These results show that Q-switched Nd:YAG laser radiation is capable of removing black crusts from limestone sculpture without removing material from the underlying stone.

Results have also been presented which show the relative inefficiency of fixed-Q laser pulses in the removal of polluted layers. In order to completely remove the black crust at a similar rate to Q-switched pulses of 1 Jcm\(^{-2}\), a fluence of 7 Jcm\(^{-2}\) was necessary. This is a consequence of thermal conduction into the bulk of the sample during the laser pulse, which appeared to lead to thermal damage of the silica grains in the surface of the sandstone.

Acoustic monitoring has also shown that, at a fluence of 0.3 Jcm\(^{-2}\), irradiation of a red Glasgow sandstone surface results in ejection of the iron oxide coating from silica grains in the surface. This gives the surface a white appearance. If Q-switched Nd:YAG laser radiation is to be used to clean red sandstone then a low fluence must be used and care must be taken to ensure that there is no alteration to the underlying stone surface.

3.6 Laser Generation of Ultrasound in Materials: Initial Experiments

Initial experiments have been carried out using a broadband PVDF-PTFE transducer to detect the generation of longitudinal elastic waves in aluminium and marble by Q-
switched Nd:YAG laser radiation. The amplitude of these waves have been measured as a function of the incident laser energy.

3.6.1 Introduction

*Ultrasound* is the propagation of high frequency elastic waves in various media. Solid media are able to support both *compressional* (longitudinal) waves, in which the propagation and displacement vectors are collinear, and *shear* (transverse) waves in which the propagation and displacement vectors are perpendicular to each other [18]. There exists other types of waves including the *Rayleigh* (or surface) wave which is confined to the surface of solids and contains both longitudinal and shear displacements so that the particle displacement is ellipsoidal. Ultrasonic energy will normally pass from one medium to another, provided the second medium is able to support the particle motion. If this is not possible, e.g. when a shear wave strikes a solid/liquid boundary, the wave may totally reflect or be partially mode converted to compressional wave energy, some of which propagates into the liquid. The passage of ultrasound across a boundary is a complex function of the angle of incidence and properties of the medium. At normal incidence the important parameter is acoustic impedance which depends on the velocity of ultrasound in the medium and the density of the medium.

Q-switched laser pulses have been used to generate longitudinal, shear and Rayleigh waves in various metals, with or without any visible surface damage to the sample [19,20]. Therefore, there exists more than one mechanism by which ultrasonic pulses are generated. As outlined in section 3.2.3, in the thermoelastic regime, i.e. at relatively low laser powers, the mechanical vibration is induced by a sudden expansion of the laser-heated region of the surface. It has been shown experimentally, that at low powers longitudinal and shear pulse amplitudes are proportional to the energy of the laser pulse, provided a constant laser pulse duration and area of irradiation of the metal surface exist [19]. Since the acoustic source has lateral dimensions (corresponding to the width of the laser beam) which are large compared to the depth of penetration into the solid it can be considered as a thin disk, as shown schematically in figure 3.26. Research has shown that the normal thermal gradient established during the laser pulse is a source of longitudinal and shear pulses, and that a major source of shear pulses is the lateral gradient [19].
As the laser power increases the nature of the ultrasonic source changes from a radial expansion to an impulse in the normal direction. Ablation of material and plasma expansion cause a momentum pulse to be transmitted to the solid, thereby enhancing the longitudinal pulse normally generated by thermal effects. The efficiency of shear pulse generation, however, is not increased with the formation of a plasma [19]. This implies that momentum effects are not a major shear generation mechanism. At high power densities, decoupling of laser energy to lateral thermal gradients within the solid due to the presence of a plasma leads to a decrease in the efficiency of shear pulse generation. Plasma shielding actually decreases both lateral and normal gradients in the acoustic source but in the case of the longitudinal pulse this effect is negligible compared to momentum transfer.

A Q-switched ruby laser has previously been used to generate wide bandwidth acoustic pulses in a range of rock samples [21, 22]. Longitudinal and shear wave velocities have been measured. This technique has also been used to study frequency-dependent attenuation and anisotropy in rocks.

### 3.6.2 Experimental Procedure

A Q-switched Nd:YAG laser has been used to generate acoustic waves in samples of aluminium and marble. Aluminium was used to characterise the transducer. A schematic diagram of the experimental arrangement is shown in figure 3.27.
The laser-generated longitudinal pulse was detected by a broadband PVDF-PTFE transducer [23]. The signals received from the transducer were averaged and the noise signal subtracted. The longitudinal pulse amplitude was measured as a function of laser pulse energy.

3.6.3 Results

In aluminium the initial longitudinal pulse and successive reflected pulses were detected. The longitudinal bulk wave velocity, $v_b$, was calculated using

$$v_b = \frac{2d}{t}$$

where $d$ is the sample thickness and $t$ is the time between the longitudinal pulse and its first reflection. A value for $v_b$ of $(6400 \pm 500) \text{ ms}^{-1}$ was calculated. This is in good agreement with the value of $6374 \text{ ms}^{-1}$ given in the 'Handbook of Chemistry and Physics' by Kaye and Laby. In marble only the initial longitudinal pulse was detected, probably as a result of scattering and strong attenuation within the sample. Figures 3.28 and 3.29 show the longitudinal pulse amplitude as a function of laser pulse energy for aluminium and marble respectively.
Figure 3.28: Longitudinal pulse amplitude as a function of laser pulse energy for aluminium.

Figure 3.29: Longitudinal pulse amplitude as a function of laser pulse energy for marble.
Direct comparisons cannot be made between figures 3.28 and 3.29 because the thickness of the samples and the quality of the coupling between the transducer and samples were different.

In the thermoelastic regime, i.e. below 18 MWcm^{-2} for aluminium and 100 MWcm^{-2} for marble, the longitudinal pulse amplitude was found to be proportional to the laser pulse energy. The rate of increase of amplitude (mV/mJ incident energy) was approximately one order of magnitude larger for marble. This is a result of the larger absorptivity at 1.06 μm of marble, 26% (see section 2.3.4.5) compared to approximately 5%. Figure 3.28 shows that once the laser power density at the aluminium surface was sufficient to form a plasma there was a rapid increase in the slope of the graph, implying an increased efficiency of longitudinal pulse generation. This is in agreement with Aindow et al [19]. Figure 3.29 shows that, in the case of marble, the onset of ablation led to a decrease in the slope, i.e. plasma formation did not enhance the longitudinal signal.

3.6.4 Conclusions

The results show that plasma formation has a different effect on the efficiency of longitudinal pulse generation in aluminium and marble:

- Aluminium; at low power densities only a small fraction of the incident energy in the laser pulse is absorbed and thermoelastic generation is inefficient. At power densities exceeding the ablation threshold, plasma shielding decreases the normal thermal gradient in the acoustic source. However, this effect is negligible compared to the momentum pulse transmitted to the solid by ablation and plasma expansion, which enhances the longitudinal pulse normally generated by thermal effects.

- Marble; at low power densities a larger fraction of the incident energy is absorbed, leading to more efficient generation of the longitudinal pulse. Above the ablation threshold, plasma shielding reduces the efficiency of longitudinal pulse generation by thermoelastic mechanisms but, in this case, momentum transfer is unable to mask this effect.

To summarise, in aluminium longitudinal pulse generation is enhanced, whereas in marble generation becomes less efficient as a result of plasma formation. This work
represents initial experiments which have been carried out to help gain a better understanding of laser-generated ultrasound in stone. Further work could be carried out to detect the longitudinal and other elastic waves generated within stone by the ablation of black crust material from its surface. It would also be useful to make quantitative measurements of the amplitudes of these elastic waves. It is believed that laser cleaning of polluted sculpture can be carried out at power densities too low for damage to result within the stone from longitudinal pulse generation.

3.7 Summary

Experiments have been carried out which demonstrate the selective nature of laser cleaning of limestone sculpture. The removal of black pollution crusts occurs via four mechanisms: (i) rapid thermal expansion, (ii) explosive vaporisation, (iii) surface relaxation and (iv) shock-induced disruption. The relative importance of each mechanism depends on the laser power density, with 'rapid thermal expansion' being more important at low powers.

The deflection of light from a probe beam by ejection of surface material from various stone surfaces has been used to measure ablation threshold fluences for clean and polluted stone. Due to the inhomogeneous nature of black crusts and stone it was necessary to quote thresholds with a corresponding probability of ablation. In general, ejection of material by Q-switched pulses occurs with a 100% probability from black crusts at a fluence half that for clean limestone surfaces. Since cleaning is usually carried out at a fluence in excess of the 100% threshold fluence for clean stone (approximately 0.025 Jcm\(^{-2}\) ) care must be taken not to remove weakly bound material from the underlying limestone surface. Ablation thresholds for fixed-Q pulses are approximately one order of magnitude larger due to thermal conduction effects.

Monitoring of the acoustic pulse generated in air as a result of material ejection from a stone surface has been shown to be a useful technique in the characterisation of laser cleaning. Results have shown that laser radiation interacts much more intensely with a strongly absorbing black crust than a weakly absorbing limestone surface. This results in more efficient removal of material from a black crust. Black crusts have been completely removed by Q-switched pulses without any visible damage to the underlying limestone. Results have also shown that irradiation of a red sandstone surface can lead to removal of the surface pigment.
Longitudinal pulses have been detected in marble. At low power densities, generation is by rapid thermal expansion of the heated region. At power densities sufficient to cause plasma formation, generation is by momentum transfer from ablated particles and plasma expansion. Above the ablation threshold, generation of longitudinal pulses in marble becomes less efficient.
References


Chapter 3: Interaction of Laser Radiation With Stone


CHAPTER 4

LASER CLEANING METHODOLOGY

4.1 Introduction

This chapter describes some of the practical techniques which have been adopted to improve the laser cleaning process. Surface analysis techniques (scanning electron microscopy and x-ray photoelectron spectroscopy) have been used to evaluate the quality of cleaning by laser as compared with conventional methods such as air-abrasive and steam. A brief review and some initial ideas for non-contact profiling of the surface are also given.

4.2 Computer Controlled Cleaning

A prototype system has been designed to clean small areas of sculpture automatically by using a computer to control the process [1]. A schematic diagram of the experimental arrangement is shown in figure 4.1. The laser beam is scanned across the sculpture using two mirrors M₁ and M₂. Movement of both mirrors in the horizontal plane scans the laser beam from left to right, whilst movement of M₁ in the vertical plane scans the beam up and down. By synchronising the firing of the laser with the controlled movement of M₁ and M₂ it is possible to clean a small area of the sculpture. The mirrors are mounted on an x-y translation stage. Movement in the x and y directions is controlled by stepper-motors which are linked, via the driver board, to a personal computer. Firing of the laser is also controlled by the driver board and computer. Parameters, such as the dimensions of the area to be cleaned, the diameter of the laser beam and the number of laser pulses per millimetre, are entered into the computer. Focusing of the laser beam is achieved using a long focal length converging lens (f = 1 m); if a short focal length lens is used variations in the surface relief of the sculpture can lead to large variations in the incident fluence.
Using this technique an area (20 mm x 35 mm) of polluted limestone was cleaned in approximately one hour, the rate of cleaning being determined by the capability of the gearboxes controlling the stepper motors. The black pollution crust (between 0.1 mm and 1.0 mm thick) was mostly removed, although where there had been a significant increase in the depth of these layers dirt remained.

It was concluded that this method of cleaning is not practical for the controlled removal of black crusts from sculpture. Due to the inhomogeneous nature of pollution crusts and the underlying stone, the variation in thickness of the crusts and the complex nature of the surface relief of many sculptures, it is not possible to completely remove the crust without damaging the stone. If too low a fluence is used then thicker parts of the crust are not removed completely, but if the fluence is too high irradiation of the underlying limestone (particularly badly damaged sections) leads to the loss of stone material. For optimum cleaning it would be necessary to use a relatively low fluence and to have a skilled conservator go back over the uncleaned areas and remove the remaining dirt with the laser beam guided through a hand-held tool. Alternatively, an image of the irradiated area could be monitored on video and the pixel intensity compared to a pre-defined value for clean stone. Irradiation of the irradiated area would continue until the pixel intensity reached the pre-defined value. However, this process would be slow and problems would be encountered with colour variations on the stone surface.
The most practical and precise method of cleaning polluted sculpture is for the conservator to have full control over the guidance of the laser beam in the form of a hand-held tool. Computer controlled cleaning might find an application in the removal of thin, uniform pollution layers (such as soot deposits) from large, flat stone walls where the underlying stone is in good condition. In such cases, where the properties of the dirt do not change significantly across the surface and irradiation of the stone will not lead to damage the surface could be uniformly cleaned by a laser system moving backwards and forwards on a rail, controlled by a computer.

4.3 The Effects of Water on Laser Cleaning

4.3.1 Introduction

It has been discovered that the efficiency of material removal from a polluted stone surface can be enhanced by applying a thin layer of water (approximately 0.1 mm) prior to irradiation. Figure 4.2 shows a polluted limestone surface which has been partially dry laser cleaned and partially wet laser cleaned. *Dry* refers to conventional laser cleaning and *wet* to laser cleaning with the addition of water.

![Figure 4.2: Dry and wet laser cleaning of polluted limestone. Magnification x4.](image)
Two 7 mm square areas of the black crust have been irradiated by a Q-switched Nd:YAG laser at 0.1 Jcm⁻². The lower area has been dry cleaned. Some of the crust has been removed but a significant amount remains, particularly within the cracks of the surface. The upper area has been cleaned by brushing a thin layer of tap water onto the surface of the crust prior to irradiation. Almost all of the crust has been removed, with only a small amount remaining in the surface cracks.

This increased cleaning efficiency has previously been observed in the removal of micron-sized particles from solid surfaces, such as silicon wafers and lithography membrane masks, by pulsed ultraviolet and infrared lasers [2,3]. It was suggested that, by depositing a transparent liquid layer onto a strongly absorbing substrate irradiation of the surface leads to very efficient heating of the liquid/substrate interface which produces superheating and explosive evaporation of the liquid film. The explosive evaporation is sufficient to overcome the forces of attraction between the substrate and particles, which are ejected from the surface. Figure 4.3 shows irradiation of a silicon surface coated by a water film.

![Diagram of particle removal by strong substrate absorption](image)

**Figure 4.3**: Illustration of particle removal by strong substrate absorption.

The effects of water on laser cleaning have been studied more closely using the scattering and acoustic monitoring techniques, described in chapter three. The absorption of water at 1.06 μm has also been measured.
4.3.2 Absorption of Laser Radiation at 1.06 μm by Water

The absorption of pulsed Nd:YAG laser radiation by water has been measured using the experimental arrangement shown schematically in figure 4.4. The energy reaching the calorimeter was initially measured with the glass cell empty. The cell was then filled with de-ionised water and the measurements repeated. There was found to be no difference in the results when tap water was used in place of de-ionised water.

![Schematic diagram of the experimental arrangement for measurement of absorption of laser radiation by water.](image)

After taking into account the reflection of a portion of the laser energy at air/glass and water/glass boundaries (see figure 4.5), and assuming no absorption by glass and air, water was found to absorb (1.2 ± 0.1)% of the pulse energy per millimetre. Hence, water is effectively transparent at 1.06 μm. A thin (0.1 mm) water film would only absorb approximately 0.1% of the incoming laser energy. For a 100 mJ pulse, incident over an area 0.2 cm², i.e. 0.5 Jcm⁻², the approximate temperature rise in the film would be 0.01°C.
Chapter 4: Laser Cleaning Methodology

4.3.3 Irradiation of a Constrained Surface

The efficiency of laser-induced longitudinal pulse generation in a solid is significantly enhanced by the presence of a transparent liquid constraining layer, such as a film of water [5-7]. This can clearly be seen in figure 4.6 which shows longitudinal pulse amplitude as a function of laser energy for both free and constrained aluminium surfaces.

A number of factors contribute to the increased generation efficiency:

- Assuming that absorption of laser energy occurs at the solid surface, by applying a thin layer of water the source has changed from being one at or very near the surface to one effectively buried within the irradiated solid. As a consequence, the acoustic source is not at a stress-free boundary and the generation of normal stresses by thermal expansion is enhanced.

Figure 4.5: Transmission of a laser pulse through a water-filled glass cell.

\[ \begin{align*}
    &1. \text{Reflection at air/glass boundary}^a \\
    &2. \text{Reflection at water/glass boundary}^b \\
\end{align*} \]

\[ ^a \text{Fraction of pulse energy reflected at normal incidence given by } \left( \frac{n_1 - n}{n_1 + n} \right)^2 \text{ i.e. } 0.04 \]

\[ ^b \text{Fraction of pulse energy reflected at normal incidence given by } \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2 \text{ i.e. } 0.004 \]
• Liquids generally have higher expansion coefficients than solids. Hence, thermoelastic stresses in the liquid, heated from the solid, exert an appreciable normal force on the solid.

• At higher powers vaporisation of the liquid exerts a momentum transfer reactive force, similar to ablation, on the solid.

![Graph](image)

Figure 4.6: Longitudinal pulse amplitude as a function of laser pulse energy for free and constrained (water) aluminium surfaces.

The effects of a constraining layer are shown in figure 4.7.

![Diagram](image)

Figure 4.7: Schematic diagram showing laser-induced stresses in a solid covered by a liquid layer.
4.3.4 Experimentation

The techniques of scattered light detection and acoustic monitoring, described in the previous chapter, have been used to study the interaction of a Q-switched Nd:YAG laser pulse with a constrained polluted limestone surface. A thin layer of tap water was brushed onto the sample surface immediately prior to irradiation.

4.3.4.1 Relationship Between Intensity of Scattered Light and Acoustic Pulse Amplitude

The intensity of scattered light has been measured as a function of the acoustic pulse amplitude at 0.8 Jcm$^{-2}$, as described in section 3.5.1. The results are shown in figure 4.8. The graph shows positive correlation, as in the case of dry cleaning, but the intensity of scattered light has increased substantially as a result of the liquid layer [8].

![Figure 4.8: Intensity of scattered light as a function of acoustic pulse amplitude for a polluted limestone surface coated by a water film.]

The intensity of scattered light detected is approximately one order of magnitude larger than that measured at the same acoustic pulse amplitude for dry laser cleaning (see figure 3.6). This is due to a combination of effects:
• Addition of a thin water layer prior to irradiation leads to increased material removal.

• Ejection of water droplets and vaporisation of water from the surface scatters the probe beam, in much the same way as the solid particles.

• There is a corresponding decrease in the amplitude of the acoustic pulse, due to the dampening effect of the liquid layer. Ejection of particles from the surface leads to the creation of an acoustic pulse in water rather than in air. The acoustic pulse is attenuated as it propagates through the water and energy is also lost by reflection at the water/air interface.

Consequently, the relationship between either intensity of scattered light or acoustic pulse amplitude and quantity of material removed from the surface is much more complex than with dry laser cleaning.

4.3.4.2 Acoustic Monitoring

The acoustic pulse amplitude has been measured as a function of the number of laser pulses during the cleaning of a polluted limestone surface (see section 3.5.2). Water was brushed onto the surface prior to irradiation. The dark grey pollution crust was approximately 0.1 mm thick.

Figure 4.9 shows the variation in acoustic pulse amplitude with number of laser pulses for wet laser cleaning. Figure 4.10 shows the results obtained for dry laser cleaning of the same surface. The acoustic pulse amplitudes are lower in the wet cleaning case as a result of the dampening effect of the water layer. The two curves are of a similar shape with an initial decrease in the amplitude followed by a levelling off as the removal process comes to a halt. However, it is clear that the acoustic pulse amplitude from a polluted surface reaches a value similar to that from a clean surface after fewer pulses when water is applied to the surface, i.e. wet laser cleaning leads to a more rapid removal of the pollution crust. In this case, the crust was removed completely after approximately 10 pulses, as compared with 30 pulses for dry laser cleaning.
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Figure 4.9: Acoustic pulse amplitude as a function of number of laser pulses for irradiation of water-coated clean and polluted limestone surfaces.

Figure 4.10: Acoustic pulse amplitude as a function of number of laser pulses for dry laser cleaning.
This increased cleaning efficiency can be clearly seen in figures 4.11 and 4.12. Figure 4.11 shows the state of the pollution crust prior to irradiation and after 10 pulses at 0.4 Jcm$^{-2}$. The crust has only been removed completely from two small areas within the irradiated region, the largest being approximately 0.5 mm in diameter. Figure 4.12 shows increased removal from the same crust at 0.4 Jcm$^{-2}$ by applying a layer of water approximately 0.1 mm thick to the surface prior to irradiation. The crust has been completely removed from the irradiated region.

Figure 4.11: Dry laser cleaning of a polluted limestone surface.

Figure 4.12: Wet laser cleaning of a polluted limestone surface.
4.3.5 Conclusions

These results have shown that the efficiency of laser cleaning is enhanced by brushing a thin layer of water onto the polluted surface immediately prior to irradiation. The water not only forms a film over the surface but is also able to penetrate into the cracks and pores of the crust. Water is effectively transparent at 1.06 µm so the laser energy is mainly absorbed by the black crust. The increased efficiency is a result of several mechanisms:

- The presence of a layer of water on a polluted surface actually improves the coupling of the incident laser energy to the black crust, i.e. more energy is absorbed by the crust due to multiple reflections at the water/air boundary. This effect can be observed optically with a darkening of the surface when water is applied.

- The constraining effect of the liquid layers can lead to more efficient generation of a longitudinal pulse, which at high powers may be sufficient to cause disruption within the crust.

- Heating of the water, from the crust, gives rise to thermoelastic stresses in the water. At higher powers heating is sufficient to cause explosive evaporation of the water (see figure 4.3). Since water penetrates into the pore space these effects exert large transient forces on particles contained in the crust. These forces are sufficient to cause loosening or even ejection of material from the crust.

Hence, by applying water to the surface laser cleaning can be carried out at a lower fluence, thereby reducing the risk of damage to the underlying stone. Once the crust has been removed and the limestone exposed heating at the water/stone interface is not so intense due to the low absorption of the stone. Water, therefore, does not enhance removal of material from a clean surface to the same extent.
4.4 Evaluation of Cleaning

4.4.1 Introduction

Conventional photography, scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) have been used to evaluate the quality of cleaning attained by Q-switched Nd:YAG laser radiation. Cleaned surfaces of limestone, marble and sandstone have been examined and, in some cases, compared to surfaces which have been cleaned by micro-abrasives. Figures 4.13 and 4.14 show a limestone surface which has been cleaned by laser radiation and micro-abrasives respectively. The surface in figure 4.14 appears much rougher as a result of overcleaning; the abrasive particles have continued to remove material from the stone surface once the polluted crust has been removed. The photographs have been taken through an optical microscope.

![Laser cleaned limestone surface. Magnification x20.](image)

The controlled nature of laser cleaning can also be clearly seen in figure 4.15 which shows a piece of polluted and badly decayed white marble, the surface of which has a sugary texture. The marble has been partially cleaned by laser radiation (right hand area) and partially by micro-abrasives (central area). The laser-cleaned surface is a light brown colour and much smoother than the abrasive-cleaned surface, which is white and rough. The laser radiation has completely removed the black pollution layer and left the patina of the marble intact. The micro-abrasives, however, have completely removed the surface layers, including the patina, thereby exposing the weakly bound and crumbling interior of the marble. This has resulted in an irreversible loss of
original material from the marble which would lead to the loss of fine detail from a sculpture and could even contribute to its accelerated decay.

Figure 4.14: Limestone surface cleaned by micro-abrasives. Magnification x20.

Figure 4.15: Comparison between laser and micro-abrasive cleaning techniques on a crumbling marble sample. Magnification x1.5.
4.4.2 Surface Analysis Techniques

4.4.2.1 Scanning Electron Microscopy

When a beam of high energy electrons interacts with a specimen their energy is dissipated, resulting in various secondary emissions from the specimen. Some of the inelastically scattered electrons are backscattered out of the specimen. One of the principal features of the scanning electron microscope (SEM) is that any radiation received from the specimen or any measurable change in the specimen can be used to provide a signal which gives rise to contrast in the image [9]. Figure 4.16 shows schematically some of the signals which can be used in the SEM.

![Diagram of signals in SEM]

Figure 4.16: Some of the signals used in the SEM.

The detection of secondary electrons and back-scattered electrons is used to study the surface features, or topography of a sample, while x-rays are used primarily for chemical analysis.

In a SEM electrons are produced, usually by thermionic emission, and accelerated to an energy between 2 keV and 40 keV. Condenser lenses are used to demagnify the electron beam until, as it hits the specimen, it has a diameter of only 2-10 nm. The fine beam of electrons is scanned across the specimen while a detector counts the number of low energy secondary electrons or other radiation given off from each point on the surface. The amplified current from the detector is used to modulate the brightness of a cathode ray tube spot which is simultaneously scanned across the screen. For effective viewing of a specimen in the SEM it is necessary for the surface of the specimen to be
electrically conducting, since during normal operation a surplus of electrons builds up on the surface. If these are not conducted away the surface acquires a negative charge and the incoming electrons are repelled and deviated from their normal path which results in a distortion of the image. Non-conducting specimens are, therefore, usually coated with a thin (~10 nm) conducting layer of gold.

In order to obtain an image in the microscope there must be a variation in the signal obtained from different parts of the specimen. Topographic images are usually obtained using secondary and backscattered electrons; as the tilt of the surface increases electrons are more likely to be scattered out of the specimen and the number of detected electrons increases. Chemical analysis can be carried out using x-rays produced by the electron beam/specimen interaction; measurement of the wavelength (or energy) of each characteristic x-ray that is emitted enables a qualitative analysis to be carried out, while measurement of the number of x-rays of any type which are emitted per second can give a quantitative analysis.

4.4.2.2 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is a technique used to give a quantitative analysis of a specimen surface. The specimen is placed in a vacuum system and irradiated with x-rays from an aluminium source. These x-rays are sufficiently energetic to cause photoemission from the core electron energy levels of the atoms present. The photoelectrons generated are collected and passed to an energy analyser. Measurement of the photoelectron energy identifies the elements present in the surface while measurement of the number of electrons per second gives a quantitative analysis. Only the photoelectrons generated near the sample surface are able to escape into the vacuum system to be detected. The sampling depth is, therefore, in the region of 3 nm.

4.4.3 Experimentation

Conventional photography, SEM and XPS have been used to analyse, both qualitatively and quantitatively, polluted stone surfaces which have been cleaned by Q-switched Nd:YAG laser radiation. The main samples studied were: red Glasgow sandstone, a white marble and a creamy brown limestone from Lincoln. For each stone polluted, clean and laser cleaned samples were analysed, initially by XPS and then using electron microscopy and EDAX (energy dispersive analysis of x-rays). Since
XPS has a sampling depth of only a few nanometres, the technique is very sensitive to matter which accumulates on the sample surface over a period of time. Adsorbed hydrocarbons, for example, are often responsible for giving misleading results about the quantity of carbon present in a sample surface. For this reason absolute values must be regarded as approximate. Accurate comparisons, however, can be made between the respective samples. The sampling depth for EDAX is a few microns and so the technique is not as sensitive as XPS to adsorbed matter. However, misleading quantitative results can arise from irregularities in the surface and for this reason EDAX has only been used to give a qualitative analysis. EDAX is unable to detect elements with an atomic number less than that of sodium (11), i.e. carbon and oxygen cannot be detected.

XPS has also been used to monitor the surface composition of polluted samples of a light brown sandstone from Lincoln cathedral which have been partially or completely cleaned by laser radiation. The results are compared with those obtained for a clean sample.

### 4.4.4 Results

#### 4.4.4.1 Lincoln Sandstone

All but one of the samples were covered by a thin black pollution crust, approximately 0.1 mm thick. The samples were exposed to different amounts of laser radiation, as shown in Table 4.1, and analysed by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polluted surface - not irradiated</td>
</tr>
<tr>
<td>2</td>
<td>1 Pulse at 0.4 Jcm(^{-2})</td>
</tr>
<tr>
<td>3</td>
<td>2 Pulses at 0.4 Jcm(^{-2})</td>
</tr>
<tr>
<td>4</td>
<td>5 Pulses at 1.5 Jcm(^{-2})</td>
</tr>
<tr>
<td>5</td>
<td>10 Pulses at 2.7 Jcm(^{-2})</td>
</tr>
<tr>
<td>6</td>
<td>Clean surface - not irradiated</td>
</tr>
</tbody>
</table>

Table 4.1: Removal of black crust material from polluted sandstone.

The quantitative results are presented in graphical form in Figure 4.17. Initially, the surface of the black crust comprised 52% carbon, 37% oxygen and 7% silicon.
of nitrogen (2%) and calcium (1%) were also present. Figure 4.17 shows that as the crust was irradiated the carbon content dropped to 22% while the oxygen content increased to 56% and the silicon content increased gradually to 16%. These results agree well with the surface composition of the clean sandstone: carbon 25%, oxygen 58% and silicon 16%. Traces of calcium, iron and sulphur were also present.

These results show clear trends in the relative amounts of carbon, oxygen and silicon present in the surface during removal of the black crust from the sandstone. The carbon content decreased, as expected, since most of the carbon is contained in the crust. The oxygen and silicon contents both increased as the silica grains became exposed, with the oxygen content increasing at approximately twice the rate of the silicon content. The additional oxygen and carbon were most probably due to adsorbed oxygen and hydrocarbons. Since the composition of the laser-cleaned sandstone agreed well with that of the clean sandstone, the analysis suggests that cleaning is carried out without any modification to the surface composition of the underlying stone.

4.4.4.2 Lincoln Limestone

Figure 4.18 shows a polluted limestone sample. The dark grey crust is less than 0.1 mm thick and XPS revealed it to be composed mainly of carbon (46%) and oxygen.
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(30%) with significant amounts of calcium (6%) and magnesium (11%) and traces of sulphur (3%), silicon (2%) and nitrogen (1%). EDAX also revealed traces of aluminium and iron.

![Figure 4.18: Polluted limestone sample.](image)

Figure 4.18 shows a polluted limestone surface which has been cleaned by laser radiation at a fluence of less than 0.3 Jcm⁻². The dirt has been removed leaving a yellow/brown surface which appears to be undamaged. This slightly darker surface (compared to the original limestone) is partly due to chemical alteration of the original stone by acid pollution. XPS revealed the surface to be composed mainly of carbon (40%) and oxygen (37%) with significant amounts of calcium (7%), magnesium (7%) and sulphur (6%). There are also traces of silicon (2%), nitrogen (1%) and iron (1%). EDAX confirmed the significant calcium and sulphur contents and also detected traces of aluminium. The results of the XPS analysis are summarised in table 4.2, which includes results for a clean limestone surface and a clean limestone surface which has been exposed to laser radiation (irradiated).

<table>
<thead>
<tr>
<th>Limestone</th>
<th>C</th>
<th>O</th>
<th>Ca</th>
<th>Mg</th>
<th>S</th>
<th>Si</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polluted</td>
<td>46</td>
<td>30</td>
<td>6</td>
<td>11</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Laser-cleaned</td>
<td>40</td>
<td>37</td>
<td>7</td>
<td>7</td>
<td>6</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Clean</td>
<td>41</td>
<td>36</td>
<td>8</td>
<td>8</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Irradiated</td>
<td>38</td>
<td>37</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4.2: XPS analysis of limestone samples showing surface composition in atomic%
As explained earlier absolute values are only approximate, with measured carbon values tending to be too high. Most of the carbon measured is due to adsorbed hydrocarbons. Comparison between the samples reveals that the polluted limestone has the largest carbon content, as expected. The results also show that the surface of the clean limestone contains as much magnesium as calcium, which suggests that the sample is actually a dolomitic limestone composed of calcium carbonate and magnesium carbonate. The sulphur content is a maximum on the laser-cleaned surface and is due to the conversion of carbonate into sulphate by atmospheric sulphur dioxide during formation of the black crust. The clean and irradiated surfaces have almost identical compositions with carbon, oxygen, magnesium and calcium present in significant quantities. This suggests that irradiation of a clean limestone surface, at a fluence suitable for cleaning, does not lead to any change in its chemical composition. The results obtained by EDAX are in agreement with the XPS analysis, although no magnesium was detected in any of the surfaces, probably a consequence of its low atomic number (12).

SEM did not reveal any differences between the topography of clean limestone and laser irradiated clean limestone. This, together with the XPS and EDAX analysis, suggests that polluted limestone can be cleaned by laser radiation without alteration to either the chemical or physical structure of the underlying stone surface. Figure 4.20 shows a micrograph of a polluted limestone surface.
SEM, however, did reveal differences between polluted limestone surfaces which had been cleaned by Q-switched and fixed-Q Nd:YAG laser radiation.

Figure 4.21 shows a polluted limestone surface which has been cleaned by Q-switched radiation. The micrograph shows that the black crust has been removed without any observable damage to the underlying stone. Figure 4.22 shows a different part of the same surface which has been cleaned by longer pulse, fixed-Q radiation. Part of the black crust has been removed but much of the limestone surface is covered by remaining dirt in shiny globular form. Some of the dirt appears to have been partially melted and upon resolidification has fused to the stone. This gives the surface a dirty, uncleaned and in some areas burnt appearance. This difference in surface appearance is a consequence of the long pulse duration of fixed-Q radiation. As energy is being deposited by the pulse, heat is conducted into the bulk of the stone. On the surface, therefore, there is sufficient energy to vaporise only some of the dirt while the remainder is raised to a temperature high enough only to cause melting. The relatively slow process of melting and fusing of the dirt may cause thermal damage to the stone.
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Figure 4.21: Q-switched laser-cleaned limestone.

Figure 4.22: Fixed-Q laser-cleaned limestone.
4.4.4.3 Red Glasgow Sandstone

Figure 4.23 shows the polluted surface of red Glasgow sandstone. The dark grey crust is less than 0.1 mm thick. XPS revealed it to be composed mainly of carbon (42%) and oxygen (39%), with silicon (11%) and traces of aluminium (3%), calcium (2%) and nitrogen (3%).

Figure 4.23: Polluted red Glasgow sandstone. Magnification ×5.

Figure 4.24 shows a polluted sandstone surface which has been carefully cleaned by laser radiation at a fluence of less than 0.3 Jcm⁻². The dark pollution layer has been removed revealing a dark red patina, partly the result of moisture movement within the stone leading to the reprecipitation of minerals on the surface. XPS revealed the surface to be composed mainly of carbon and oxygen, with a significant amount of silicon and traces of calcium and nitrogen. Part of the carbon detected was due to dirt left on the surface but the majority was attributed to adsorbed hydrocarbons. Figure 4.25 shows a clean sandstone surface composed of carbon (17%), oxygen (50%) and silicon (24%) with traces of aluminium (6%), nitrogen (2%) and calcium (1%). Oxygen and silicon are present in the ratio 2:1, which is as expected for a surface composed mainly of silica. However, surprisingly, no iron was detected.
EDAX confirmed the presence of silicon and traces of aluminium and calcium in the surface and also detected potassium and iron in each of the samples. The iron can be attributed to the iron oxide powder which coats many of the silica grains and gives the surface a red colour. XPS was unable to detect iron in all but one of the samples, most probably as a result of carbon on the surface. This meant accurate comparisons between samples could not, unfortunately, be made. XPS did not give
Figure 4.26: Polluted red sandstone.

Figure 4.27: Laser-cleaned red sandstone.
meaningful results for a clean surface which had been irradiated at 0.3 Jcm⁻², but it was apparent that the resulting surface appeared lighter than that shown in figure 4.25, due to partial removal of the iron oxide pigment. EDAX showed silicon to be present with traces of aluminium, potassium, calcium and iron. Figures 4.26 and 4.27 show micrographs of the polluted sandstone and laser-cleaned sandstone samples respectively. Removal of the pollution crust has made the silica grains more distinct. Some dirt remains in the intergranular space. There appears to be no damage to the surface. SEM did not reveal any differences between the topography of clean sandstone (figure 4.28) and laser irradiated clean sandstone (figure 4.29). This suggests that over-irradiation of a clean red sandstone surface simply leads to removal of the iron oxide pigment without any further modification to the stone surface.

![Clean red sandstone](image)

**Figure 4.28: Clean red sandstone.**

Laser radiation can be used to remove layers of dirt from this type of sandstone without damaging the underlying patina. However, extreme care must be taken since irradiation of the clean surface at too high fluence leads to removal of the pigment and a subsequent modification to the surface appearance.
4.4.4.4 White Marble

Unfortunately, it was not possible to carry out XPS analysis on the marble samples due to their badly decayed crumbling state. Figure 4.30 shows a polluted marble surface. The thin layer of dirt is approximately 0.1 mm thick. Figure 4.31 shows a sample of the same stone which has been cleaned by laser radiation. The dirt layer has been completely removed revealing a smooth light brown surface, characteristic of the altered surface of calcareous stones exposed to a polluted atmosphere. The fine surface detail of sculpture is often preserved in this altered layer so it is desirable to maintain it intact. Micro-abrasive cleaning of the same sample successfully resulted in removal of the surface dirt but also removed most of the altered layer beneath, thereby exposing the crumbling interior of the marble.
Figure 4.32 is a micrograph of a polluted marble surface. Figure 4.33 shows the same pollution crust at increased magnification. The crust appears to be partly composed of gypsum crystals. Figure 4.34 is a micrograph of a different area of the same crust at high magnification. This shows the heterogeneous nature of the crust. It is composed of many particles and crystals of different shapes and sizes, originating from various sources, including power station emissions and car exhaust fumes. Figure 4.35 is a micrograph of a clean marble surface.
Figure 4.32: Polluted marble surface.

Figure 4.33: Polluted marble surface. Increased magnification.
Figure 4.34: Spherical particles found in a polluted marble surface.

Figure 4.35: Clean marble.
Figures 4.36 and 4.37 show laser-cleaned and microabrasive-cleaned marble surfaces, respectively. A difference between the two surfaces is apparent: the crust formed by alteration of the original marble surface as a result of exposure to atmospheric sulphur dioxide remains on the laser-cleaned surface, but has been removed from the abraded sample. Figure 4.38 shows a clean marble surface which has been exposed to laser radiation; the left side at a fluence (2.5 Jcm\(^{-2}\)) in excess of the damage threshold and the right side at a fluence (0.5 Jcm\(^{-2}\)) below the damage threshold which corresponds to a fluence which might be used during cleaning. There is no observable damage to the right side but damage is obvious on the left where excessive energy has been deposited in the surface region leading to ablation of surface material. This clearly shows the damage which can result if cleaning is carried out by an unskilled operator with no understanding of the processes involved.

Figure 4.36: Laser-cleaned marble.
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Figure 4.37: Microabrasive-cleaned marble.

Figure 4.38: Clean marble surface, left side of which has been irradiated at 2.5 Jcm\(^{-2}\) and right side at 0.5 Jcm\(^{-2}\).
4.4.5 Conclusions

Surface analysis techniques (SEM, XPS and EDAX) have been successfully used in conjunction with conventional photography to provide useful information about the state of cleaned stone surfaces. The results have shown that cleaning techniques using laser radiation are more refined than those using micro-abrasives. Laser radiation allows the conservator to remove layers of dirt from a sculpture surface whilst maintaining the underlying altered layer intact. This preserves surface detail and prevents, particularly in badly decayed sculpture, exposure of weakly bound crumbling stone material which in an aggressive environment will accelerate decay of the object. Cleaning of limestone, sandstone and marble surfaces can be carried out without any apparent alteration to the chemical or physical structure of the stone surface. At excessive fluences, however, modification to the surfaces can result. In the case of red sandstone this modification is in the form of a colour change due to removal of the iron oxide pigment. In the case of marble and limestone the topography is modified as stone material is ablated. These results emphasise the importance of skill and understanding of the processes involved if laser cleaning is to be used to its full potential. This is especially true for the cleaning of red sandstone since modification to the underlying stone can result at relatively low fluences.

This work has also shown the care with which results must be interpreted, as shortcomings were found in each of the surface analysis techniques. At high magnification SEM only looks at a very small area of the surface of the sample and so care must be taken to ensure that the area being observed is typical of the surface as a whole. XPS is highly sensitive to adsorbed hydrocarbon layers which can mask elements which are present in the surface of the sample. EDAX is unable to give an accurate quantitative analysis of an irregular surface and is unable to detect the presence of carbon, oxygen and, in this instance, magnesium. If used alone, each of these techniques could lead to misleading results. However, when the techniques are used together and the results carefully analysed, useful information about the chemical and physical state of a stone surface can be obtained.

4.5 Surface Profiling: Initial Experiments

To help evaluate the quality of cleaning by different methods it would be useful to obtain profiles of cleaned surfaces using some kind of non-contact profiling technique. Several possible techniques are considered.
4.5.1 Holographic Interferometry

Holography can be used to produce three dimensional images of diffusely reflecting objects which appear to be overlaid by interference fringes, supplying information about deformation, displacement or rotation of the object [10].

*Double-exposure* holographic interferometry has been used to detect detached areas in paintings [11]. If a painting suffers some kind of deformation the detached and non-detached regions are expected to behave differently. By making a hologram of the painting, slightly heating the surface of the painting in-situ and exposing the hologram once more, the detachments are revealed as local changes in the holographic interference pattern.

*Multiple-source* holography has previously been used for artwork erosion measurements [12]. The underlying principle is the illumination of the object with a light source which can change in position or frequency during the exposures, thereby creating two separate and independent holograms. On reconstruction, two separate wavefronts are generated and interfere to produce a reconstructed image with superimposed contours which can be used for profile, depth, long term wear and corrosive surface changes. This form of holographic contouring is currently being developed to measure surface variations on wooden panels [13].

These techniques have possibilities in the non-contact profiling of stone surfaces. However, holographic measurements are strongly affected by the presence of external noise, such as mechanical vibrations and air turbulence, and the process is relatively time consuming due to development of the holographic plates. A system has been developed in which this problem is overcome by recording the hologram using a video camera rather than a photographic plate [14]. This technique is currently being used to detect changes occurring to a stone surface over a period of time. An initial hologram of the surface is made and stored in solid-state memory. A second hologram is made of the surface and subtracted from the first. If the surface has moved or changed at all in the time between the two frames then the result of the subtraction is a contour map with lines linking areas of the object which have moved the same distance. Each of these techniques presents information about the surface in the form of fringe patterns, which have to be interpreted. This can be a complicated process.
4.5.2 Auto-Focus Technique

This technique of surface profiling makes use of the phase-matching system now employed in many auto-focus cameras. A beam of light entering the camera through the taking lens is first focused in the neighbourhood of the film plane. It is then divided into two image-forming rays which are projected onto two CCD image sensor arrays. If the subject is in focus then the images fall on the same relative parts of the sensor arrays giving rise to outputs which are in phase. However, if the subject is out of focus then the rays fall on different relative positions creating a phase difference in the output signals.

By scanning the system across a stone surface and using the amount of defocus as a measure of the surface height at regular intervals an accurate map of the surface relief could be obtained. Initial experiments have been carried out, using the auto-focus module from a Pentax camera, to investigate the feasibility of this technique. A schematic representation of an experimental arrangement is shown in figure 4.39. A pinhead was illuminated as the object. An image of the pinhead was formed in the vicinity of the infrared filter by the taking lens. This image was split into two and projected onto the CCD array of a CCD camera by the separator lenses. A television monitor was used to display the images. Several taking lenses were used to study the vertical movement of the pin necessary to produce a detectable change in the horizontal separation of the two images on the monitor.

Figure 4.39: Schematic diagram of experimental arrangement used for investigating the possible use of an auto-focus module to profile a stone surface.
It was found that by increasing the object distance \( u \) the two images moved closer together. This was due to a decrease in the image distance \( v \) as shown in figure 4.40.

\[ \begin{align*}
\text{Taking lens} \\
\text{Separator lens} \\
\text{CCD Arrays}
\end{align*} \]

Figure 4.40: Diagram showing the movement of images due to a change in object distance.

The maximum sensitivity of the system was obtained using a 50 mm microscope objective as the taking lens. Such a lens gave a 1 mm change in \( dx \) for a vertical displacement of 0.25 mm.

This technique has been shown to work in principle. However, to be of use in profiling the surface of stone, the sensitivity of the system would have to be increased by at least one order of magnitude. This might be possible with larger magnification microscope objectives, but as the focal length of the lens is reduced there is a corresponding decrease in the depth of field which might limit the resolution. It would be relatively straightforward to design a system incorporating the auto-focus technique to measure changes in surface height of a well-defined object. However, the profiling of a rough stone surface is a much more complicated problem.

### 4.5.3 Stereophotography

*Stereophotography* is a technique which has been used for many years to record sculpture where conventional two dimensional photography has not proved satisfactory. Stereoscopic photography reproduces the phenomena of *binocular* vision,
where separation of the eyes by a small horizontal distance enables the viewer to see two slightly different aspects of near objects, which the brain interprets in terms of distance and mass. The sensation of depth can be simply recreated by making two photographs of the same scene from slightly different positions which are viewed in such a way that each eye sees the appropriate print at a distance approximately equal to the focal length of the camera lens. The distance between the positions from which the photographs are taken is made equal to the interpupillary distance, assumed to be 65 mm when the pupils are fixed on an object at infinity. A common form of viewing stereoscopic slides uses two pairs of polarising filters to separate the two images. The two slides are projected onto a non-polarising screen. One pair of filters is used on the projector lenses and one pair in the form of glasses. In stereoscopic projection the filters are so arranged that the image seen by the left eye cannot be seen through the filter placed over the right eye and vice-versa.

Stereophotography has been looked at as a possible technique for providing qualitative information about stone surfaces. Stereoscopic pairs of slides of laser-cleaned stone surfaces were taken using different camera lenses, varying the separation between camera positions and varying the object distance. The slides were viewed by stereoscopic projection.

With an object several metres away an increased sense of depth was obtained using a 35 mm lens rather than a 135 mm lens. This was due to the increased viewing angle of the 35 mm lens which is used at a shorter object distance. Viewing of the object was most comfortable with a stereoscopic pair taken with a separation of 30 mm. With a separation of 65 mm the stereoscopic effect was good, but viewing was tiring on the eyes. With a separation of 90 mm it was not possible to bring the two images close enough to be viewed comfortably, making the eyes diverge to create a sensation of depth. It was important to use a small aperture to ensure every part of the object was in focus since any blurring of the image becomes a major distraction to the eye when viewed on a screen. Using a small aperture it was important to illuminate the object sufficiently to capture as much detail as possible.

Best stereoscopic results for the detailed study of a stone surface were obtained using a 135 mm lens and a reduced lateral separation of only 10 mm between exposures. In this situation a minimum aperture was used to obtain maximum depth of field.

Stereoscopic photography provides more information about the size, shape and texture of stone sculpture than conventional two dimensional photography. When used to
examine a stone surface in detail this technique can provide valuable qualitative information about the state of the surface. One disadvantage is that the observer must wear special glasses.

4.5.4 Conclusions

The development of a non-contact technique, with a resolution of 0.01-0.1 mm, to accurately profile a stone surface would be useful for the evaluation of the quality of cleaning achieved by different methods. At present it is not clear whether holographic and auto-focus techniques could be developed to provide practical methods of obtaining quantitative information about the state of a stone surface, although both methods appear promising. Stereophotography provides a practical means of recording qualitative information about the state of a stone surface.

4.6 Summary

This chapter has described some of the practical techniques which have been adopted to enhance the efficiency of laser cleaning and some of the techniques employed to evaluate the quality of cleaning. The most practical and precise method of cleaning sculpture is for the conservator, rather than a computer, to have full control over the guidance of the laser beam in the form of a hand-held tool. Surface analysis techniques used in conjunction with photography have shown that laser radiation provides the conservator with a more refined method of cleaning sculpture than micro-abrasives. Cleaning by laser would, therefore, extend the life of the object. Results have also shown, however, that laser cleaning is a skilled technique and if carried out in a haphazard fashion will result in damage to the object. By applying a thin layer of water to the object immediately prior to irradiation the cleaning efficiency can be enhanced; removal of dirt can be carried out at a lower fluence than with dry laser cleaning, thereby reducing the risk of damage to the object.
References


CHAPTER 5

LASER BEAM DELIVERY

5.1 Introduction

Due to the size, weight and cooling requirements of a Nd:YAG laser and its power supply, its use as a cleaning tool requires a beam delivery system to accurately guide the laser beam to the point of interest on the sculpture. Two possible delivery systems have been considered: (i) a fibre optic system and (ii) an articulated arm system. Experiments have been carried out to select the most suitable system for cleaning sculpture. This work has led to the development of a flexible, hand-held laser cleaning tool which can be used by conservators either in the laboratory or on site.

5.2 Laser Beam Delivery by Optical Fibres

5.2.1 Introduction

Light can be guided within a fibre as a result of the phenomenon total internal reflection. When an electromagnetic wave is incident upon the boundary between two dielectric media, whose refractive indices are \( n_1 \) and \( n_2 \), then in general a portion of that wave is reflected and the remainder transmitted, according to the Fresnel equations [1]. Figure 5.1 illustrates this case.

![Diagram showing total internal reflection](image)

Figure 5.1: Illustration of the behaviour of electromagnetic radiation at the boundary between two dielectric media.
It can be shown [1] that when $\theta_i > \theta_c$, where $\theta_c$ is the critical angle given by

$$\theta_c = \sin^{-1} \left( \frac{n_2}{n_1} \right)$$

total internal reflection is observed, i.e. there is no transmitted wave in the second medium. The refractive index profile for a *step index* fibre waveguide is shown in figure 5.2.

![Refractive index profile for a step index waveguide.](image)

The cladding refractive index is $n_2$, the core refractive index is $n_1$ and the core radius is $a$. The path of a meridional ray, i.e. a ray that passes through the centre of the fibre, entering a step index fibre and undergoing total internal reflection is shown in figure 5.3. The angle $\alpha$ that the ray entering the fibre makes with the normal to the end of the guide is related to the internal angle $\theta$ by Snell's law,

$$\frac{\sin(\alpha)}{\sin(90^\circ - \theta)} = \frac{n_1}{n_0}$$

Hence

$$\sin(\alpha) = \frac{n_1}{n_0} \cos(\theta)$$

The maximum value that $\alpha$ can take is, therefore, determined by the minimum value that $\theta$ can take which is the critical angle $\theta_c$. Thus,

$$n_0 \sin(\alpha_{\text{max}}) = n_1 \left(1 - \sin^2(\theta_c)\right)^{1/2} = (n_1^2 - n_2^2)^{1/2}$$

where $(n_1^2 - n_2^2)^{1/2}$ is known as the *numerical aperture* (NA) of the fibre.
This gives

\[ \alpha_{\text{max}} = \sin^{-1}\left(\frac{\text{NA}}{n_0}\right) \]

where \( \alpha_{\text{max}} \) is the fibre acceptance angle and defines the maximum entrance angle of a ray which will be transmitted along the fibre. Only certain values of \( \theta \) are allowed [1], each one being associated with a distinct wave pattern or mode within the waveguide (c.f. modes within a laser cavity). The number of modes that can be propagated is proportional to the fibre radius.

![Diagram](image)

**Figure 5.3:** Illustration of the path of a meridional ray on entering a circular step index fibre.

Single mode fibres are of great importance in optical fibre communications; for transmission of radiation at 1 \( \mu \)m along a fibre, assuming typical values of refractive index, the maximum radius for single mode operation is 1.27 \( \mu \)m. With high power applications, where energy transmission rather than beam quality is important, multimode operation is more appropriate and fibre radii of several hundred microns are common.

The use of fibres to guide low power continuous laser beams has many applications, including communications. During the last ten years there has been a growing interest in fibre applications requiring very high power transmission. These have included laser-based optical firing systems to initiate explosives [2], high power optical fibre sensors [3,4], medical applications of lasers [3,4] and generation of high amplitude stress waves in materials [3,5].

Transmission of high power laser pulses through a fibre is not straightforward, since the rapid deposition of laser radiation into a dielectric can lead to damage and breaking of the fibre. Since high power radiation is often transmitted at power densities close to
the damage threshold for the core of the fibre, conditions must be as near to perfect as possible for successful transmission. Research has shown [2] that probable sites for laser-induced damage are: (i) the front face, (ii) the entry segment, (iii) the rear face and (iv) at locations of high stress resulting from bends introduced to the fibre. Commercially available fibres can reliably transmit Nd:Glass laser pulses of high power density (3.5 GWcm\(^{-2}\)) without bulk or surface damage [3]. The damage threshold for a given fibre diameter was found to be more dependent on the characteristics of the input laser beam (such as hot spots in the beam profile) than on fibre properties, such as cladding material and numerical aperture. The highest limits were obtained with a high-divergence, multimode input beam, which has been attributed to filling a relatively large number of propagation modes of the fibre. It is not unusual for the surface of a fibre to damage at one half to one third the energy density required to damage its bulk [6]. Dust on the surface of a fibre has been found to lower the damage threshold by a factor of two [4]. Surface quality and hence the nature of the surface preparation of the fibre are, therefore, very important.

Research has shown that fibre damage thresholds can be increased by: (i) immersing the input end of the fibre in a few millimetres of water [4,7] and (ii) laser conditioning the input face of the fibre [2,4,6]. By covering the fibre surface with an index matching fluid surface features are filled and no longer scatter incoming radiation. Electric field intensifications due to surface imperfections are, therefore, partially relaxed and the likelihood of surface damage reduced. Annealing a surface with a continuous CO\(_2\) laser can raise the damage threshold by a factor of 3-4 [4], although it is not yet clear whether this effect is permanent [2]. It is believed that the enhanced performance of CO\(_2\)-polished surfaces results from two mechanisms [6]: (i) the microcracks caused by mechanical polishing are healed by heating and (ii) the contaminated surface layer is vaporised away.

Alternatives to using an ordinary single fibre to transmit high power laser radiation include: (i) a tapered fibre [3] and (ii) a fibre bundle [5]. Fibre tapers are convenient for many applications, since they can provide high optical intensities at the output of a fibre while having less stringent requirements for alignment at the input. By forming a number of fibres into a bundle the energy in the laser beam is shared between all of the fibres, rather than being transmitted along a single fibre. The likelihood of fibre damage is, therefore, reduced.
To summarise, there are many factors which can contribute to damage of optical fibres during transmission of high power laser radiation. Some of the mechanisms of laser induced damage in optical materials are briefly outlined in the following section.

5.2.2 Laser Induced Damage in Transparent Solids

The formation mechanisms of laser induced damage in a transparent solid can be divided into two categories [8]: (i) extrinsic damage and (ii) intrinsic damage.

**Extrinsic** damage refers to damage caused by the presence of surface defects or contaminants, such as highly absorbing microscopic inclusions, impurity and bulk clusters, particles of abrasive materials and adsorbed materials from the atmosphere. Each of these defects can be strongly absorbing and give rise to local heating of the host material. Damage arises either from mechanical failure, such as buckling or cracking, or from thermal failure, such as melting or vaporisation.

**Intrinsic** damage refers to damage on the surface or in the bulk of a pure material. It is believed that damage in such materials is related to the electric field of the incident radiation. On the surface of a pure sample the enhanced electric field associated with the presence of defects such as scratches, voids and cracks is responsible for laser induced damage. In the bulk of a pure sample the sequence of events which lead to damage are believed to be as follows:

(i) At a sufficiently high fluence the electric field intensity is strong enough, not only to accelerate electrons initially in the conduction band but also, to ionise valence band electrons from the host material.

(ii) Once in the conduction band these electrons help to ionise more electrons, which causes the absorption of the sample to increase.

(iii) As the absorption increases the temperature of the sample increases and at some point irreversible changes, such as melting or fracture, leading to damage will occur.
5.2.2.1 Damage Testing of Fused Silica

In order to estimate the diameter of fibre necessary to transmit high power laser radiation at energy levels suitable for cleaning polluted sculpture the single shot damage threshold of a fused silica sample was measured.

The sample was a 6 mm thick disc. The output from a Q-switched Nd:YAG laser (6 ns, 250 mJ) was focused by a 100 mm convex lens. The sample was placed beyond the focal point of the lens and slowly moved towards the laser until damage was observed. Damage was assumed to occur when a visible plasma formed. The results must, however, be treated with caution since it has been shown that the development of damage does not necessarily imply the formation of a plasma [9].

The lowest fluence at which damage to the sample was certain to occur was found to be between 3.8 and 5.0 Jcm⁻², i.e. between 0.6 and 0.8 GWcm⁻². However, the single shot damage threshold is typically over twice that for multiple pulse irradiation [8], so values of 0.3 and 0.4 GWcm⁻² are more appropriate here.

Assuming a silica fibre to have a damage threshold of 0.3 GWcm⁻² these results suggest that successful transmission of 100 mJ pulses would require a diameter of at least 2.5 mm. Such large fibres are very expensive and relatively stiff compared to normal flexible fibres of less than 1 mm diameter. It was decided that for a practical fibre optic delivery system it would be necessary to either use a tapered fibre or a fibre bundle.

During the experiment it was observed that on each occasion the sample damaged at its rear face first. This result is in agreement with Crisp et al [9] who have shown that interference between incident and reflected radiation at the surfaces of a transparent dielectric material significantly influences surface damage thresholds. For normal incidence, radiation that is reflected at the entrance face is 180° out of phase with the incident radiation and the resulting destructive interference causes a sizeable decrease in the electric field at the entrance face. Radiation reflected at the exit face suffers no phase shift and constructive interference with the incident radiation slightly enhances the electric fields experienced at the exit face. Damage is, therefore, expected to occur first at the exit face.
5.2.3 Experimentation

Experiments have been carried out using a tapered silica fibre. The core material was a high purity silica and the coating material a two layer polymer. The specifications of the fibre are listed below:

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input core diameter</td>
<td>3.25 ± 0.05 mm</td>
</tr>
<tr>
<td>Input cladding diameter</td>
<td>3.40 ± 0.05 mm</td>
</tr>
<tr>
<td>Output core diameter</td>
<td>1.50 ± 0.05 mm</td>
</tr>
<tr>
<td>Output cladding diameter</td>
<td>1.60 ± 0.05 mm</td>
</tr>
<tr>
<td>Taper length</td>
<td>0.5 m</td>
</tr>
<tr>
<td>Pigtail length</td>
<td>2.5 m</td>
</tr>
<tr>
<td>Numerical aperture</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Launch of the laser beam into the fibre was achieved by fitting a brass attachment, which held the fibre entrance face and focusing lenses in position, to the output of the Q-switched Nd:YAG laser. For efficient energy transmission it was required that the laser beam pass through the centre of the lenses and entrance face of the fibre. Burn paper was used to locate the beam in the near and far fields. The beam was found to exit the output aperture of the laser 3 mm below the centre and at an angle of 0.6° from its axis (see figure 5.4).

![Figure 5.4: Direction of propagation of laser beam with laser viewed side on.](image)

This problem was overcome by tilting the front plate forwards slightly and fitting an extra plate to the laser to effectively raise the laser beam by 3 mm, as shown schematically in figure 5.5.
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Figure 5.5: Modifications to the laser aperture for beam direction to be along the axis of the coupling lenses and entrance face of the fibre.

To reduce electric field intensifications due to surface imperfections and Fresnel reflections the entrance and exit faces of the fibre were immersed in water.

Initially, a single planoconvex lens was used to launch the laser beam into the fibre. The focal length of the lens was calculated using the numerical aperture of the fibre and the diameter of the laser beam. The maximum acceptance angle of the fibre immersed in water was calculated using

\[ \alpha_{\text{max}} = \sin^{-1} \left( \frac{\text{NA}}{n_0} \right) \]

where NA is the numerical aperture and \( n_0 \) is the refractive index of water. Hence \( \alpha_{\text{max}} = 10.4^\circ \). Ideally, to give efficient energy transmission through the fibre, the focal length of the lens used would be defined by \( \alpha_{\text{max}} \) as shown schematically in figure 5.6. In this case the focal length of the lens in water \( f_w \) would be calculated using

\[ f_w = \frac{r}{\tan(\alpha_{\text{max}})} \]

where \( r \) is the radius of the incoming laser beam, giving

\[ f_w = \frac{3}{\tan(10.4^\circ)} = 16.3 \text{ mm} \]
It should be remembered that the focal length of a planoconvex lens half-immersed in water is dependent on which surface is immersed and that the focal length of the same lens in air is shorter.

![Diagram of laser beam focusing through planoconvex lens]

**Figure 5.6:** Focusing of the laser beam using a single planoconvex lens to fill a large number of propagation modes of the fibre.

The arrangement shown in figure 5.6 is not appropriate for launching a high power laser beam into a fibre, since the beam would be brought to a focus within the fibre giving rise to permanent damage. The fibre was, therefore, positioned after the focal point of the lens so that the beam was diverging as it entered. However, by bringing the beam to a focus in water before the fibre breakdown occurred (at pulse energies of approximately 50 mJ, c.f. 100 mJ in air). This resulted in poor energy transmission through the fibre, since a large proportion of the energy contained in the laser pulse was lost in the formation of a plasma. The problem of breakdown was overcome by using a planoconvex and a planoconcave lens in combination to form a *beam reducer*, as shown schematically in figure 5.7.

![Diagram of lens combination to launch laser beam without breakdown]

**Figure 5.7:** Lens combination to launch laser beam without breakdown in air or water.
One concern with this arrangement was whether the converging beam produced by the convex lens would damage the front face of the concave lens. To investigate this a glass slide was used to simulate the front face of the lens. Its damage threshold was found to be between 6 Jcm\(^{-2}\) and 11 Jcm\(^{-2}\), which was sufficiently high to suggest that damage would not occur during the launching of the laser beam into the fibre. The lens combination was required to reduce the beam diameter by a factor of about one third. To produce a collimated beam of 2 mm diameter the following criteria must be satisfied:

\[
\frac{f_1}{f_2} = 3 \quad \text{and} \quad d = f_1 + f_2
\]

where \(d\) is the lens separation and \(f_2\) is negative. To avoid convergence of the laser beam inside the fibre it was decided to make \(f_1 > 3f_2\) so that a slightly diverging beam entered the fibre. Lenses were chosen so that \(f_1 = 160\) mm and \(f_2 = -40\) mm. The path of the emerging beam from the second lens was verified using Snell’s law, as shown in figure 5.8.

Figure 5.8: Schematic representation of refraction of the laser beam at the front face of a diverging lens.

The angle \(\alpha\) of the incoming ray to the optical axis is given by

\[
\alpha = \tan^{-1}\left( \frac{r}{f_1} \right) = \tan^{-1}\left( \frac{3}{160} \right) = 1.07^\circ
\]

The radius of curvature of the diverging lens \(r_2\) is given by
\[ r_2 = (n - 1) f_2 = (1.519 - 1) \times 40 \text{ mm} = 20.76 \text{ mm} \]

Hence,

\[ \theta = \tan^{-1} \left( \frac{1}{20.76} \right) = 2.76^\circ \]

The angle of incidence of the incoming ray \( i \) is given by

\[ i = \alpha + \theta = 1.07 + 2.76 = 3.83^\circ \]

The angle of the refracted ray \( r \) is given by Snell's law so that

\[ \frac{\sin i}{\sin r} = 1.519 \Rightarrow r = 2.52^\circ \]

The ray will, therefore, be refracted slightly towards the normal on passing into the lens. The angle of incidence \( i_2 \) of the ray at the rear face is given by

\[ i_2 = \theta - r = 0.24^\circ \]

The angle of emergence \( r_2 \) of the ray from the lens into water is given by

\[ \frac{\sin i_2}{\sin r_2} = \frac{1.333}{1.519} \Rightarrow r_2 = 0.27^\circ \]

The laser beam is, therefore, diverging slightly as it exits the lens combination, as shown schematically in figure 5.9.

Glass \( n=1.519 \)  
Water \( n=1.333 \)

Figure 5.9: Path of an emerging ray from the lens combination.
A single planoconvex lens was used to focus the output from the fibre. The output was assumed to be diverging from a point $O$ at an angle $\theta$ defined by the numerical aperture of the fibre, as shown schematically in figure 5.10.

![Diagram of focusing of output energy from fibre](image)

**Figure 5.10: Focusing of the output energy from the fibre.**

Since

$$\frac{1}{f} = \frac{1}{v} + \frac{1}{u}$$

$$\frac{1}{v} = \frac{1}{f} - \frac{1}{u}$$

Hence, for the emerging rays to be brought to a focus to the right of the lens, i.e. for $v$ to be positive, the condition $f < u$ must hold. The lens must, therefore, have a sufficiently short focal length and a large enough diameter to capture all of the emerging laser radiation and bring it to a focus. A lens with $f = 31.5$ mm and a diameter of $25$ mm was chosen. The lens was oriented, as in figure 5.10, so that when the output face of the fibre and the front surface of the lens were immersed in water the effective focal length of the lens was kept to a minimum.

### 5.2.4 Testing of the Fibre

The fibre was tested using the arrangements shown schematically in figures 5.11 and 5.12. The energy emerging from the final focusing lens was measured using a Gentec calorimeter and compared to the energy per pulse measured directly from the laser.
The fibre was initially tested at a repetition rate of 0.5 Hz. The energy per pulse from the laser was measured at 215 mJ. The output from the fibre was measured as 64 mJ at the beginning of the experiment and after 1500 pulses, i.e. there had been no deterioration in energy transmission through the fibre. Approximately 30% of the energy per pulse emitted by the laser was transmitted through the fibre and system of lenses. Most of the losses can be accounted for by absorption in water (see section 4.3.2) and reflection at air/glass and water/glass boundaries. With the arrangements shown in figures 5.11 and 5.12 the theoretical maximum transmission is 41%, with 80% transmitted at the entrance and 51% at the exit. This compares favourably with the measured values for transmission of 67% and 45% at the entrance and exit respectively. The major part of the discrepancy between theoretical and measured values was most probably a result of absorption by unclean surfaces, attenuation by the fibre and inefficient coupling of radiation into the fibre. By redesigning the output of the system to reduce the length of water to 7.5 mm it would have been possible to increase the theoretical maximum transmission to approximately 64%.

Rugged testing of the fibre was carried out at the same energy level but at a repetition rate of 5 Hz for 1.25 hours. The output energy was measured after approximately
22500 pulses and was found to be zero. There was no damage to the exit face of the fibre, but damage was observed in the form of a chip and a circular mark on the entrance face with a crack which began at the cladding interface and propagated approximately 4 mm along the edge of the fibre. Figure 5.13 shows the undamaged exit face of the fibre. Figure 5.14 shows the damaged entrance face of the fibre after rigorous testing.

![Figure 5.13: Undamaged exit face of the fibre. Magnification ×12.](image1)

![Figure 5.14: Damaged entrance face of the fibre. Magnification ×8.](image2)

Damage was also observed in the form of a 1 mm diameter hole which had been drilled through the centre of the diverging lens used in the beam reducer. It was not clear whether the fibre had damaged as a result of, or independently of, the damaged lens.
Two possible causes of lens damage were: (i) surface contamination and (ii) rod lensing. Any strongly absorbing dirt or dust particles on a lens surface can give rise to intense localized heating which can result in permanent damage. Rod lensing is an effect which is sometimes observed when lasers are operated under rigorous conditions. At high repetition rates a thermal gradient is established within the laser rod, since heat cannot be dissipated so readily within the rod as on its surface. The temperature gradient can give rise to changes in the divergence of the laser beam with the rod itself beginning to act like a weak lens. At 5 Hz this effect may have been sufficiently strong to focus the beam onto the surface of the diverging lens. To test this hypothesis the damaged lens was replaced with a glass slide and the laser was run at 5 Hz for 1.5 hours. No damage to the slide was observed suggesting that surface contamination rather than rod lensing was responsible for damage to the lens.

As stated earlier, damage to the fibre may have resulted from damage to the lens. Imperfections in the lens would have led to increased scatter of the laser beam, possibly giving rise to hot spots on the fibre surface which would induce melting and cracking. The collection of debris from the lens on the fibre surface would have a similar effect. These effects would explain damage to the fibre surface. However, the crack within the fibre is more likely to have been caused by hot spots appearing as a result of fibre/laser misalignment [4]. Once a crack appears it tends to propagate readily.

5.2.5 Conclusions

A tapered silica fibre successfully transmitted 64 mJ pulses of Q-switched Nd:YAG laser radiation at a repetition rate of 0.5 Hz. This is sufficient, when focused, to remove many black encrustations from polluted sculpture, but at a rate of only 0.5 Hz cleaning would be painstakingly slow. At a more practical repetition rate of 5 Hz permanent damage to the entrance face of the fibre and one lens occurred resulting in transmission of zero energy. It is not clear whether damage to the fibre occurred independently of the damaged lens. It is clear, however, that a combination of surface contamination and misalignment of the fibre did contribute to the damage. This work has shown that the guidance of a high power laser beam by an optical fibre, at repetition rates suitable for cleaning, requires perfectly clean optical surfaces and perfect laser/fibre alignment. For cleaning sculpture, a laser is likely to be operated under rigorous conditions and in a relatively dirty environment. These results, therefore, suggest that a tapered fibre would not provide a practical and reliable means
of beam delivery. A fibre bundle may provide a more reliable delivery system. However, increasing the number of fibres would also increase the stiffness of the system, thereby reducing its effectiveness in cleaning delicate and intricate sculpture.

5.3 Laser Beam Delivery by Mirrors

5.3.1 Introduction

Specially coated mirrors and prisms can be used to guide high power laser beams without many of the problems associated with fibre optics. By incorporating mirrors into an articulated arm system comprising a series of hollow aluminium tubes, or arms, joined together by elbow units, a laser beam can be accurately guided to the point of interest on an object. A single elbow unit, incorporating two mirrors, is shown schematically in figure 5.15. By rotation about two axes a single unit is able to guide a laser beam to any point on the inside surface of an imaginary sphere centred on the elbow.

![Figure 5.15: Cross-section showing guidance of a laser beam through a single elbow unit.](image)

In order to clean sculpture in a precise and careful manner it is necessary to control: (i) the distance between the hand-held tool and the surface and (ii) the angle between the focused laser beam and the surface. This can be achieved by using a delivery system which incorporates a total of six mirrors and three elbow units, as shown schematically in figure 5.16.
Each pair of mirrors is incorporated in a single elbow unit

Direction of mirror rotation

Laser beam enters delivery system

Figure 5.16: Schematic representation of an articulated arm beam delivery system showing the orientation and direction of rotation of each mirror.

The aluminium arms have an internal diameter of approximately 25 mm, which is sufficiently large for the diverging laser beam to pass cleanly through the delivery system.

5.3.2 Experimentation

A Q-switched Nd:YAG laser was mounted vertically on a trolley. An articulated arm laser beam delivery system, purchased from Spectron Lasers, was positioned directly above the output aperture of the laser and clamped in position by two brackets. The system is shown being used to clean a marble bust in figure 5.17. The diverging laser beam is focused as it exits the delivery system by a converging lens fixed inside a pen-
like handpiece. The intensity of the laser beam incident on a surface can, therefore, be controlled by varying the distance between the tool and surface.

Figure 5.17: Laser cleaning of a marble bust.
5.3.2.1 Alignment of Laser Beam and Delivery System

In order for a laser beam to pass unaffected through an articulated arm the laser must be precisely aligned with the axis of the arm. Any inaccuracies in alignment will result in relative movement between the beam and the centre of the output, and in severe cases reflection from the internal walls of the arm during rotation. Such effects give rise to unexpected movement of the beam as it emerges from the delivery system during cleaning. To compensate for the downward slanting beam emitted from this particular laser (see section 5.2.3) an aluminium wedge was fitted between the laser and the aluminium channel. For guidance a visible HeNe laser was precisely aligned with the Nd:YAG laser, in the near and far fields.

For approximate alignment a 10 cm long hollow tube was fitted in place of the articulated arm. Plugs with 2 mm diameter centre holes were fixed in either end of the tube and steel shims were wedged beneath the fixing brackets until the HeNe beam passed through the centre of both holes.

The tube was more accurately aligned using the arrangement shown schematically in figure 5.18. The glass plate was assumed to have parallel faces. Initially, the plane mirror was adjusted to return the guidance beam back through the output aperture of the HeNe laser. The position of the tube was carefully adjusted until each of the visible spots resulting from weak reflections at the glass surfaces disappeared through the pinhole in the white card.

Figure 5.18: Side view of the experimental arrangement used to accurately align the articulated arm.
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The final alignment procedure involved replacing the tube with the articulated arm and aligning each of its six mirrors, one at a time. The procedure for the first mirror is shown schematically in figure 5.19. The rest of the delivery system was removed and a plane mirror used to reflect the HeNe beam back into the Nd:YAG laser. Mirror 1 was adjusted to return the beam back through the pinhole and to eliminate movement of the reflected spot during rotation of the arm. This was repeated for each mirror in turn until the delivery system had been reassembled.

![Diagram of laser beam delivery system](image)

Figure 5.19: Schematic representation showing the procedure for mirror alignment within the articulated arm.

5.3.3 Results

Following the alignment of the laser and arm, using procedures described in the previous section, the laser beam wandered no more than 5 mm from the centre of the output during rotation of any or all of the sections of the arm. It was decided that this was sufficiently accurate for cleaning purposes. The system has since been used to clean sculpture both in a laboratory environment and in situ on the external fabric of buildings. Tests have been carried out at energies of up to 300 mJ and at repetition rates of up to 10 Hz for several hours without any deterioration in the output of the system.

5.3.4 Conclusions

The articulated arm provides an efficient and practical means of laser beam delivery for the cleaning of polluted sculpture. Techniques for accurate alignment of the laser and arm have been described and a system has been developed which provides the
conservator with a flexible, precise and refined tool, for use either in a laboratory or on site.

5.4 Summary

Low power laser beams can be guided by either optical fibres or mirrors. The successful transmission of high power laser pulses through a fibre, however, requires perfect laser/fibre alignment and perfectly clean optical surfaces, since the power densities involved are close to the damage threshold of silica. A tapered fibre has been used to reliably transmit pulses of up to 64 mJ at a repetition rate of 0.5 Hz. However, when operated under conditions similar to those encountered when cleaning sculpture the fibre was permanently damaged. It seems likely that a fibre bundle would transmit high power pulses more reliably, but the use of several fibres leads to a sharp increase in the stiffness and cost of the delivery system. This work has shown that fibre optics are not suitable for guiding high power laser pulses in the cleaning of polluted sculpture.

The use of specially coated mirrors to guide high power laser pulses, however, has been shown to be reliable and practical. Alignment requirements are less stringent than with fibres and an articulated arm provides a rugged and flexible beam delivery system. Up to 300 mJ pulses have been transmitted at repetition rates of 10 Hz without any deterioration in output. A Q-switched Nd:YAG laser with an articulated arm delivery system provides the conservator with a practical tool capable of cleaning polluted sculpture in a very precise and controlled manner.
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References


CHAPTER 6

CONCLUSIONS AND FURTHER WORK

This work suggests that the development of cleaning techniques which use laser radiation to remove dirt and corrosive products will make a significant contribution to the refinement of conservation technology. The process of removing dirt from deteriorated sculpture by laser radiation has been shown to be less damaging than comparable chemical and abrasive techniques. By reducing the damage caused by cleaning processes not only is the life expectancy of objects increased but it also becomes possible to select the type of accretions which are removed from their surfaces.

The removal of black crusts from stone sculpture is necessary for aesthetic reasons and to ensure better preservation of the object. Conventional cleaning techniques have often proved successful in restoring the outer appearance of an object but, by their very nature, damage to some extent will always occur. It is not possible to completely remove a strongly bound layer of dirt from deteriorated stone by mechanical methods without causing collisions between abrasive particles and the stone surface. Once a chemical is applied to a surface penetration into the bulk of the stone ensures that reactions cannot be closely monitored and controlled. Traces of the chemical will always remain. If these techniques are employed skilfully then damage to the object may only be caused on a microscopic scale. However, in extreme cases where techniques have been employed carelessly and inappropriately damage in the form of loss of material, staining and mineral depletion not only contributes to disfigurement but also to accelerated decay, thereby shortening the life of the object. Laser radiation is able to remove layers of dirt from sculpture without any mechanical contact and without the use of potentially hazardous chemicals. Cleaning can, therefore, be carried out in a very controlled manner.

It has been shown that a Q-switched Nd:YAG laser (6 ns, 1.06 μm) is the most suitable type of laser for the cleaning of polluted marble and limestone surfaces. Measurements have shown that black crusts resulting from atmospheric pollution typically absorb between 2.5 and 3.5 times as much of the incident radiation at 1.06 μm as typical clean limestone and marble surfaces. Measurements of ablation thresholds, by deflection of a probe beam, revealed material to be removed from a black crust at a
fluence approximately half that required to remove material from a clean limestone or marble surface. Hence, at low fluences the removal of polluted layers by laser radiation is self-limiting, in that once the dirt has been removed continued irradiation of the stone surface does not result in loss of material. Monitoring of the acoustic pulse, generated in air as a result of material ejection from a stone surface, has been shown to be a useful technique in the characterisation of laser cleaning. The technique has shown that, as expected, laser radiation interacts much more intensely with a strongly absorbing black crust than a weakly absorbing limestone surface resulting in more efficient material removal from a black crust. The removal of black crust material occurs via a combination of four mechanisms: (i) rapid thermal expansion, (ii) explosive vaporisation, (iii) surface relaxation and (iv) shock-induced disruption. The relative importance of each mechanism is dependent on the laser power density, with rapid thermal expansion having greater importance at low powers.

Laser-cleaned surfaces have been analysed qualitatively and quantitatively using conventional photography, SEM, XPS and EDAX. The results have shown that cleaning techniques employing laser radiation are more refined than techniques using micro-abrasives. Laser radiation allows the conservator to remove the polluted layers whilst maintaining the patina of the stone intact, so preserving surface detail and protecting the underlying weakly bound material from exposure to an aggressive environment. Results have also shown that laser radiation is able to remove polluted layers without any apparent alteration to either the physical or chemical structure of the underlying stone.

Water has been shown to enhance the removal of material from a black crust. Hence, by applying a thin layer of water to the surface immediately prior to irradiation laser cleaning can be carried out at a lower fluence, thereby reducing the risk of damage to the underlying stone.

A Q-switched Nd:YAG laser has been developed into a practical cleaning tool by using a series of mirrors incorporated in an articulated arm to accurately guide the laser beam. A single tapered silica fibre was unable to reliably transmit such high power laser pulses at repetition rates suitable for cleaning sculpture. Laser radiation provides a precise and controlled means of cleaning polluted sculpture. The technique is not only more refined than conventional cleaning methods but also has considerable advantages in the area of health and safety; it does not generate a large volume of dust particles, nor does it produce toxic chemical vapours. This allows conservators increased control over their work and also makes working in public places easier. However, some
precautions must be taken: safety glasses must be worn at all times and the laser beam must be enclosed to avoid the possibility of injury from stray reflections. The conservator must be familiar with laser safety and an extractor should be used to remove matter ejected from the surface of the sculpture. Despite the self-limiting nature of laser cleaning the final quality of cleaning achieved is dependent on the skill of the conservator. In the hands of a skilled conservator who understands the technique and is aware of its strengths and limitations laser radiation can be used to clean the most fragile of sculpture without any loss of surface material. However, if used haphazardly laser cleaning can result in severe damage to the surface of any sculpture.

It should be remembered that a Nd:YAG laser has been developed primarily to clean polluted limestone and marble sculpture. Initial tests have also been carried out in which laser radiation has been successfully used to remove polluted layers from terracotta and Glasgow and Rosslyn sandstones, graffiti and black cement from limestone and corrosion layers from brass. Figures 6.1 - 6.9 show limestone sculpture from Lincoln Cathedral which has been partially cleaned by Q-switched Nd:YAG laser radiation. Cleaning has been carried out at a rate comparable to that of abrasive cleaning. Figures 6.1 - 6.3 show a badly decayed head which was initially covered by a black pollution crust varying in thickness between 0.1 mm and 2 mm. The left side of the head and part of the nose have been broken off, revealing the friable state of the underlying limestone. The crust has been successfully removed from the face and upper half of the right ear. The quality of cleaning is excellent; polluted layers have been removed from a very fragile surface without damaging the underlying patina. Cleaning has accentuated surface features, such as the eye, hair and upper part of the mouth, which were hidden by the crust. Cracks visible on the cleaned surface were initially present beneath the crust and do not appear to have been enlarged, which further demonstrates the controlled nature of the process.
Figure 6.1: Polluted limestone head (approximately 20 cm high) from Lincoln Cathedral.

Figure 6.2: Laser-cleaned limestone head. Polluted layers have been left on the lower half of the right ear.
Figure 6.3: Close-up of the cleaned area around the eye and nose.

Figures 6.4 - 6.6 show a gargoyle which has been partially cleaned by laser radiation. The region around the nose beneath the nostrils and the left side of the face, including the eye, hair and ear, were initially covered by a rough pollution crust varying in thickness between 0.1 mm and 1.0 mm. Removal of the crust has revealed the original texture of the surface and the poor friable condition of much of the sculpture, with sections of stone material peeling away from the surface. The upper part of the nose is white, compared to the pale brown of the cleaned stone, due to rain washing. In its original orientation, on the outside of the cathedral, dirt only collected in the areas sheltered from direct rainfall. Regions such as the upper part of the nose were exposed to the elements and continually washed during rainfall.
Figure 6.4: Partially cleaned gargoyle (approximately 40 cm high) from Lincoln Cathedral.

Figure 6.5: Close-up of the cleaned areas below the nostrils and lower part of the nose. The upper part of the nose appears white due to rain washing.
Figure 6.6: Close-up of the cleaned areas on the left side of the face, showing an eye, ear and hair.

Figures 6.7 - 6.9 show a grotesque from which part of the thick black crust has been removed entirely by laser radiation. The hard crust is as thick as 4 mm in places and completely obscures the shape and texture of the limestone surface. The most practical method of cleaning such a polluted sculpture would be to use abrasives or scalpels to remove most of the crust mechanically and laser radiation to remove polluted layers close to the surface of the stone. The crust has also been partially removed from the mouth to reveal a tooth.
Figure 6.7: Partially cleaned grotesque (approximately 70 cm high) from Lincoln Cathedral. The thick crust has been removed from the lower part of the front revealing the texture of the surface.
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Figure 6.8: Close-up of the profile of the grotesque prior to cleaning.
Figure 6.9: Close-up of the profile of the grotesque after partial cleaning. A small section of the crust has been removed to reveal a tooth.

Figure 6.10 shows a friable piece of limestone, half of which was initially covered by a black cement. Black cement has been used in the past to hold decaying stone together. However, it makes consolidation of the underlying stone very difficult and destroys the aesthetic qualities of the stone. The removal of such layers by conventional cleaning techniques is very difficult, since the cement is very hard and the underlying stone is often in a friable condition.

Figure 6.10: Black cement on friable limestone. The cement has been partially removed by laser radiation.
As a result of strong absorption by cement at 1.06 \( \mu \)m laser radiation was able to remove the unwanted layers without further damaging the limestone.

Figure 6.11 shows an Ancaster limestone surface from which spray paints have been partially removed by laser radiation. With the exception of blue paint, which appears to act more like a dye in that it stains the surface, the pigments have been removed without damaging the underlying limestone. However, the surface of the stone has been darkened in areas from which the pigment has been removed. It appears as if the pigment in the paint has been removed by a process similar to the removal of black crusts by laser radiation but that the binder in the paint remains, darkening the stone as a result of a change in the optical properties of the surface.

![Figure 6.11: Removal of graffiti from a limestone surface by laser radiation. The pigment is ablated but the binder remains.](image)

Figures 6.12 and 6.13 show a marble bust which has been partially cleaned. Laser radiation has removed smooth black pollution layers, approximately 0.25 mm thick, from the hair, neck and right shoulder of the bust, without any damage to the underlying marble.
Figure 6.12: Partially cleaned marble bust (approximately 40 cm high).
Figure 6.13: Close-up of the hair, showing the dividing line between polluted marble and laser-cleaned marble.

Figures 6.14 - 6.17 show a sample of eighteenth century terracotta which has been removed from the outside of the Henry Cole wing at the Victoria and Albert Museum in London. The sample was initially covered by a black layer of dirt, between 0.1 mm and 0.25 mm thick, composed mainly of fine carbon particles. In some areas the terracotta has been severely weathered so that the hard fire skin has been lost. This can be seen where the surface is pitted and along the flat surface where, over a period of years, running water appears to have washed away the skin from one half (the surface appears rougher and lighter). Removal of the protective skin leads to accelerated decay of the sculpture. The sample has been successfully cleaned by laser radiation; the dirt has been removed without damaging the remaining fire skin. The actual state of the terracotta can now be more closely studied to allow decisions to be made to ensure the preservation of the sculpture.
Figure 6.14: Polluted and weathered terracotta sample (approximately 20 cm long).

Figure 6.15: Laser-cleaned terracotta. Layers of soot have been removed without further damaging the protective fire skin.
Figure 6.16: Close-up of the terracotta sample showing soot deposits and effects of weathering.

Figure 6.17: Close-up of the laser-cleaned area showing no damage to the remaining fire skin.
Figures 6.1 - 6.17 clearly demonstrate the precise and controlled nature of laser cleaning. They also show that laser radiation is not limited to the removal of black crusts from marble and limestone, but that it can also be used to remove a whole range of materials, including cement and paint, from surfaces as different as terracotta and sandstone. As long as laser radiation interacts more intensely with the substance to be removed than the underlying surface controlled cleaning should be possible.

Further work should be carried out to investigate the suitability of Nd:YAG laser radiation for cleaning other types of stone sculpture, such as different types of sandstone, granite and coloured marble. Stone is a heterogeneous material; the properties of one block of limestone can vary considerably from another block of limestone even if they were quarried in the same area. As much information about the properties and history of the stone should be obtained before laser cleaning is carried out. The properties of laser radiation suggest applications in the cleaning of materials other than stone, including: metals, plaster, paper, textiles, stained glass and painted surfaces. The interaction of different types of laser radiation with different materials should be studied in order to select the most appropriate laser for each application, e.g. Nd:YAG radiation was able to remove the pigment in spray paint from stone, but left the binder on the surface; an excimer laser operating in the ultraviolet might be more effective in removing both the pigment and the binder, thereby restoring the stone more closely to its original appearance.

Scope for further work also exists in improving the understanding of the laser radiation/stone interaction. It is believed that four mechanisms contribute to the removal of material from a polluted stone surface, the relative importance of each one depending on the laser beam intensity. Work should concentrate on evaluating the contribution of each mechanism to the ablation process. Schlieren techniques could be used to qualitatively and quantitatively analyse the shock waves formed in air during the interaction and to analyse their effects on surface material. A more detailed study of the formation and propagation of ultrasonic waves within stone during ablation would help to improve understanding of the cleaning process. Transducers could be designed and employed to detect shear and Rayleigh waves. Quantitative measurements of the different ultrasonic wave modes, though difficult to carry out in a strongly attenuating material such as stone, would supply information about the proportion of energy coupled into the stone and the depths to which the wave modes propagate.
Development of a non-contact surface profiling technique with a resolution of 0.1 - 0.01 mm would provide a useful means of evaluating and recording the quality of cleaning achieved and would allow straightforward comparisons between different methods of cleaning. The development of a sensing device to feed back information to the conservator or a computer about the colour, brightness or texture of the surface being cleaned would help to make the cleaning process even more controlled. This would be particularly useful in precise cleaning of small areas of pigmented stone. At present, if pigment is known to be present on a stone surface cleaning must be carried out very slowly and carefully. If the pigment is strongly absorbing at 1.06 μm then irradiation may lead to its removal, so the final quality of the surface is determined solely by the skill of the conservator. Automatic cut-out of the laser when directed at pigment would help to ensure that the pigment could not be mistakenly removed.

Refinements to the prototype laser would include the addition of a footswitch for safety and practical reasons and incorporation of a guiding beam in the system to aid aiming of the Nd:YAG beam. This thesis has described the development of a Nd:YAG laser primarily to clean polluted sculpture. Recently a lot of interest has been expressed by stone cleaning companies in the possibility of developing a laser-cleaning system for work on large areas of stone work. For this application the speed of cleaning becomes more important. Further work could look into the feasibility and practicality of using a more powerful laser and spreading the beam over a larger area to clean more rapidly. The maximum cleaning rate attainable would, most probably, be determined by practical considerations, such as the size and weight of the system, cooling requirements and safety aspects. Initial calculations suggest that at present these limitations would be reached using a 1.2 J Q-switched Nd:YAG laser. Such a laser would be capable of cleaning approximately ten times faster than the current system, i.e. it would be possible to remove layers of soot approximately 0.25 mm thick from a smooth terracotta wall at a rate of 1 - 2 cm²s⁻¹.

In conservation the rate of cleaning is of secondary importance to the quality. The prime objective is to remove dirt as carefully as possible in order to restore the object to its former glory and to extend its life. Any loss of material from an object is irreversible. The precision and control provided by a laser make it an ideal tool for the cleaning of sculpture. With rising concern over the damage caused by conventional cleaning techniques, laser cleaning has a valuable and increasingly important role to play in conservation.