The evaluation of laser cleaning of stone sculpture
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ABSTRACT

A Q-switched Nd:YAG laser has been developed to clean polluted stone sculpture. Results are presented showing the controlled manner in which polluted layers are removed from the sculpture without damage to the underlying stone. The absorption of laser radiation at 1.06μm by a black encrustation has been shown to be three times that of a clean limestone surface. Measurements of the threshold laser fluence (energy density) for surface material removal show that there exists a range of fluence within which it is possible to clean the sculpture without damage to the stone surface. The amplitude of the shock pulse generated in air by the sudden ejection of material from the polluted surface has been monitored to show that as the stone is exposed the laser pulse has a negligible effect on the surface.

INTRODUCTION

The formation of unsightly and damaging black encrustations on stone monuments due to interaction with atmospheric pollution has become an all too familiar problem. Traditional cleaning techniques, such as particle abrasion and liquid jets, have often proved successful in restoring the outer appearance of a sculpture. However, by their very nature these techniques damage the underlying stone and often result in the loss of fine detail from a sculpture.

Whilst working in Venice in 1972 it became apparent to Asmus and co-workers (Asmus [1]) that laser radiation is able to selectively vaporise layers of dirt from decaying marble sculpture. A Nd:YAG laser was later used in several conservation projects in Venice (Asmus et al [2,3,4]). However, at that time lasers were expensive and conventional cleaning techniques provided a more practical and affordable solution. At Loughborough, a Nd:YAG laser is being developed into a practical cleaning tool which can be used in a very precise and controlled manner to remove black encrustations from stone sculpture in various states of decay. Research has shown that a Q-switched Nd:YAG laser
(wavelength 1.06 μm, pulse length 20 ns) is the most suitable form of laser radiation for the cleaning of sculpture (Cooper [5]). The technique allows removal of the encrustation without damage to the patina of the stone in a way not possible using conventional techniques.

This paper presents results which demonstrate the very controlled nature in which dirt is removed from the sculpture whilst preserving the state of the underlying stone.

EXPERIMENTAL

1. Absorption of Laser Radiation at 1.06 μm by Clean and Polluted Stone

A matt or rough surface reflects radiation diffusely. An ideal diffuse reflecting substance scatters the incident radiation according to

\[ I(\text{obs}) = I(o) \cos(\alpha) \cos(\beta) \]

where:
- \( I(o) \) is incident intensity
- \( I(\text{obs}) \) is reflected intensity
- \( \alpha \) is angle of observation
- \( \beta \) is incident angle of radiation

This gives rise to the circular distribution of reflected radiation seen in figure 1.

If the sample being considered is a diffuse reflector then by measuring the radiation reflected at an angle \( \theta \) and comparing this with that reflected from a reference sample at \( \theta \), it is possible to calculate the proportion of incident radiation, \( R \), reflected from the sample. Assuming no transmission the absorptance of the stone, \( A \), can then be calculated using

\[ A = 1 - R \]
A fast integrating photodiode was used to measure the distribution of reflected radiation from different stone surfaces. All measurements were made in the plane of incidence of the laser pulse. The Nd:YAG laser supplied low energy pulses with a pulse length of 100 µs to ensure no removal of material from the sample. Each sample was verified as a diffuse reflector and compared to the reference. The reference sample was a white diffuse reflecting tablet of co-dried aluminium hydroxide and magnesium carbonate, assumed to have \( R = 1 \). Results are presented in table 1.

<table>
<thead>
<tr>
<th>Stone</th>
<th>Clean Surface</th>
<th>Patina</th>
<th>Black Crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ancaster Limestone</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lincoln Sculpture 1 (Limestone)</td>
<td>0.30</td>
<td>0.56</td>
<td>0.92</td>
</tr>
<tr>
<td>Lincoln Sculpture 2 (Limestone)</td>
<td>0.28</td>
<td></td>
<td>0.88</td>
</tr>
<tr>
<td>Lincoln Sculpture 3 (Limestone)</td>
<td>0.20</td>
<td></td>
<td>0.89</td>
</tr>
<tr>
<td>White Marble</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glasgow Sandstone (Blonde)</td>
<td>0.44</td>
<td></td>
<td>0.86</td>
</tr>
<tr>
<td>Glasgow Sandstone (Red)</td>
<td>0.58</td>
<td></td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 1: Absorptance of several clean and polluted stone surfaces at 1.06 µm

The results show that a black encrustation absorbs approximately three times as much incident radiation at 1.06 µm as clean limestone. Clean sandstone samples absorbed slightly more radiation than clean limestone samples but still significantly less than a black encrustation. White marble absorbed only 6% of the incident radiation. These results can be used to show that a pulsed laser is capable of selectively vaporising a black encrustation from stone. The temperature rise at a surface after time, \( t \), due to a high power laser beam is given by (Ready [6]),

\[
T(0,t) = \frac{2AI_0\sqrt{kt}}{K\sqrt{\pi}}
\]

where
- \( A \) is surface absorptance
- \( I_0 \) is incident power density
- \( k \) is thermal diffusivity
- \( K \) is thermal conductivity

For the purpose of these calculations it has been assumed that the black encrustation is composed entirely of carbon, with an absorptance of 0.9. To
raise the temperature of the irradiated crust to 3700 °C (at which temperature carbon sublimes) using a Q-switched Nd:YAG laser would require a fluence of ~0.1 Jcm$^{-2}$. The same fluence would result in a temperature rise of ~770 °C on the surface of limestone ($A = 0.3$) which, assuming to be composed of calcite, decomposes at ~900 °C. The corresponding temperature rise for a marble surface ($A = 0.1$) would be only 260 °C.

Due to inhomogeneities in chemical composition and structure of stone and polluted layers it is not possible to accurately calculate the temperature rise at a surface due to absorption of laser radiation. However, these results clearly show that the difference between the absorptance of the encrustation and the absorptance of stone is an important factor in the selective removal of polluted layers from stone sculpture.


Pulsed laser radiation at 1.06 μm (100 μs pulse length) was focused onto the surface of the sample. A red Helium Neon (HeNe) laser beam was passed across the surface of the sample at the same height as the Nd:YAG laser pulse, thereby interacting with any material ejected from the surface. The HeNe beam was focused onto a knife edge placed between the focusing lens and a CCD video camera, as shown in figure 2.

![Figure 2: Experimental arrangement for detection of material ejected from surface](image-url)
As the laser energy is increased a point is reached (threshold fluence) at which the fluence is sufficient to remove material from the sample. Material which is ejected scatters HeNe light predominantly towards the camera and the event is viewed as a series of bright specks moving rapidly across the monitor. The threshold fluence was determined at ten different sites on the sample and the probability of material removal at each fluence calculated. The sample was a limestone sculpture with clean and polluted surfaces from Lincoln Cathedral. Results are shown in figure 3.

![Graph showing probability of material removal from a stone surface against incident laser fluence](image)

**Figure 3:** Results showing probability of material removal from a stone surface against incident laser fluence

The results show that there exists a range of fluence (0.75 - 1.26 Jcm\(^{-2}\)) within which there is a 100 % probability of removing material from a black crust and a 0 % probability of removing material from the clean limestone. Exposure of limestone to laser radiation once the black crust has been removed will, therefore, not result in removal of surface material.

3. **Acoustic Measurements of the Laser Cleaning of Stone Sculpture**

The rapid ejection of material from a stone surface causes a shock pulse in the air which is audible as a snapping sound and detectable by a transducer. Q-switched Nd:YAG laser radiation was focused onto the surface of a sculpture to give an incident fluence of 1 Jcm\(^{-2}\). The shock pulse generated by the interaction of the laser pulse with the stone was detected by a microphone and the corresponding voltage signal measured on an oscilloscope. The shock pulse
amplitude was measured as a function of the number of laser pulses for both clean and polluted stone surfaces. Results are presented in figure 4.

The results clearly show the efficiency of 1.06 µm laser radiation in the removal of material from a polluted stone surface. The shock pulse amplitude rises to a maximum during removal of the black crust. After approximately ten pulses the amplitude begins to decrease as the underlying limestone is exposed and less material is removed. Figure 4 also shows the corresponding curve for a clean limestone surface. The maximum amplitude is much smaller than that obtained with the black crust. Some signal is still observed as the fluence of 1 Jcm⁻² is above the threshold value for material removal from a clean limestone surface.

SUMMARY

Results have been presented which show the controlled manner in which Q-switched Nd:YAG laser radiation is able to remove polluted layers from stone sculpture. Absorption of 90 % of the incident laser radiation by polluted layers gives rise to a large and rapid temperature increase. Some material is raised to a temperature beyond its boiling point and is vaporised. Large forces induced in the crust by rapid thermal expansion of material within a confined volume can also lead to the breaking of bonds and subsequent ejection of material. Once the black crust has been removed only about 30 % of the incident radiation is
absorbed by the limestone. Provided the laser fluence is below the threshold for material removal from limestone, the absorbed energy is insufficient to cause damage. The laser, therefore, provides a very precise and controlled means of cleaning stone sculpture. Air-abrasive cleaning often leads to removal of surface layers from the underlying stone since the abrasive is unable to distinguish between the black crust and stone.

Figure 5 shows a limestone head from Lincoln Cathedral which has been cleaned by Q-switched Nd:YAG laser radiation. Sections of the black crust have been left on the ear and nose to show the state of the sculpture prior to cleaning. Parts of the head have decayed to such an extent that they crumble when touched. Laser radiation is able to clean such a sculpture without causing further damage.

![Figure 5: Laser-cleaned limestone sculpture](image)

Other techniques being used to investigate the laser cleaning process include Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) to look at the structure and chemical composition of surface layers during cleaning. Initial results show there is no change to the chemical composition of the stone as a result of the removal of polluted layers by laser radiation (Cooper [7]). Transducers are presently being used to study the generation of ultrasonic waves within stone by laser radiation.
ACKNOWLEDGEMENTS

This project is carried out under the CASE programme of SERC and one of us (MIC) is in receipt of an SERC research studentship.

REFERENCES


