**Laser Techniques and Systems in Art Conservation**
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# Underlying Mechanisms in Laser Techniques for Art Conservation: Two Improved Cleaning Methods

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## ABSTRACT

Optimisation of restoration techniques employing lasers is dependent on the selection of laser wavelength, cover fluid, pulse duration and method of application. This affects the mechanisms operating during the removal process and hence its efficiency. The risk of unwanted side effects will be more or less controllable depending on the mechanism of removal.

This paper reviews laser removal mechanisms relevant to art conservation and outlines experimental work on the cleaning of polluted marble while employing two new cleaning methods: angular removal and laser shock processing.

These two new methods both show clear advantages over conventional cleaning at normal incidence. A model for each method is proposed and the improvement in performance is quantifed. The relevance of the new techniques to art conservation is clearly outlined.

Keywords: Laser cleaning, mechanisms of cleaning, angular cleaning, laser shock cleaning

## 1. INTRODUCTION – BACKGROUND ON CLEANING MECHANISMS

A schematic summary of the various mechanisms available in laser cleaning and an indication of the operating window for each is shown in Figure 1. Each regime is briefly discussed in turn. A new variant in the application of these techniques (angular cleaning) and a new mechanism (laser shock cleaning) as developed by the authors are then discussed.

### 1.1 Selective vaporisation

From his work on the laser cleaning of stone and marble using a ruby laser [1-7], Asmus concluded that there are two principal cleaning mechanisms. In normal pulse mode (pulse duration approximately 1μs - 1 msec), at relatively low laser intensity ($10^3$ - $10^5$ W/ $cm^2$) cleaning occurred as a result of the selective vaporisation of the surface contaminants compared with the underlying material which remained almost wholly unaffected. This in turn occurred when the absorption coefficient of the darker encrustation was sufficiently large to lead to a temperature rise favouring vaporisation while the absorption coefficient of the underlying material was sufficiently small to limit temperature rises to moderate values that did not allow the occurrence of cracking (as a result of differential thermal expansion), melting or vaporisation - conditions that are frequently obtained with dark encrustations on marble or stone. It was shown that a one dimensional heating model could account for the difference in the surface temperature increase between two layers with different absorptivity to the incident laser energy. A more detailed review of this work is available [8].

### 1.2 Spallation

In practice, the selective vaporisation mechanism has been little applied in laser cleaning of art works, largely because of the relatively high temperature that is reached by the substrate despite the selective absorption effect and the relative slowness of the process. Shorter pulses such as those delivered by Q-switched Nd:YAG lasers induce less substrate heating and were found to offer faster rates of contaminant layer removal.

In Q-switched mode (pulse duration approximately 5-20 nsec) a spallation (termed by Asmus an ablation) mechanism was suggested to be responsible for the cleaning effect. At this high flux level ($10^7$ - $10^{10}$ W/ $cm^2$), even relatively reflective surfaces absorb sufficient energy to reach the vaporisation temperature. High temperatures (typically $10^4$ - $10^5$ K) are produced in the vaporised material produced from the surface or the ambient gas and at these temperatures this vapour becomes partially ionised and absorbs the laser energy strongly. The initial surface vaporisation stops as the target is shielded from the laser by the partially ionised ("plasma") vapour. As the pulse continues, the vapour is further heated and high pressures (1 - 100 Kbar) can be produced, resulting in a shock wave which produces microscopic compression of the surface of the target material. When the laser pulse ends, the plasma expands away from the surface, the material surface relaxes and a thin surface layer (1-100 µm) is removed resulting in spallation. Whilst cleaning is more rapid in this case, there is a greater propensity for damage to the material underlying the surface encrustation that requires removal. For pulsed laser radiation, two relatively distinct regimes have been observed [9 - 15] - a laser surface combustion (LSC) regime which tends to be favoured at low intensity and a laser surface detonation (LSD) regime which is favoured at higher intensity.

In addition to these two mechanisms proposed by Asmus, there are other laser /materials interaction phenomena that can result in surface cleaning.

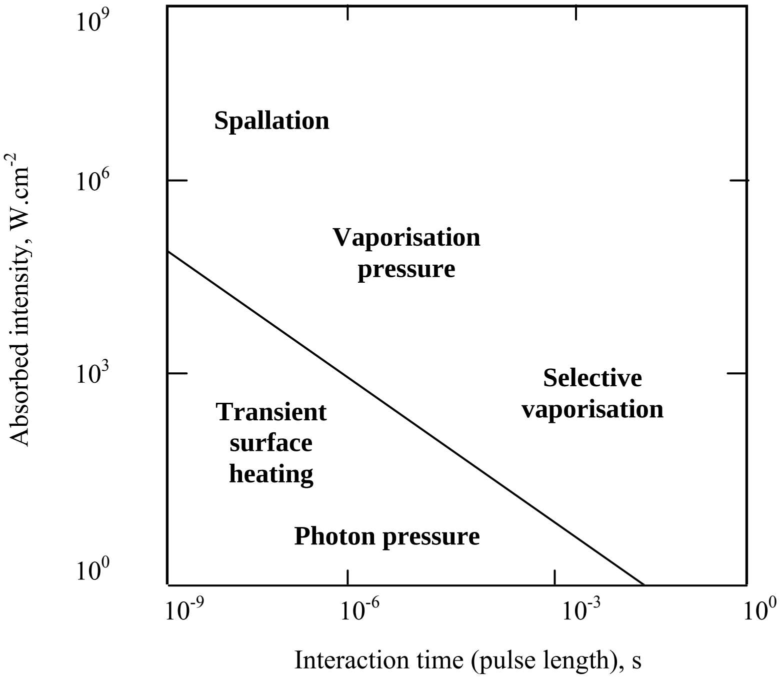

Figure 1. Absorbed intensity versus interaction time diagram showing schematic regimes of candidate laser cleaning mechanisms

### 1.3 Transient surface heating

There is evidence that shock waves may be formed simply as a result of the very rapid heating and cooling of the irradiated surface as a result of interaction with a short laser pulse. The magnitude of the effect is sufficient that initially generated thermoelastic stresses can generate acoustic waves.

A number of workers have observed the effect of short pulse lasers in generating thermoelastic stresses in the surface of solids [16-21]. Ready [22], clearly distinguishes such a transient surface heating mechanism from others where material is removed from the surface by evaporation. When laser radiation is deposited rapidly and absorbed by the surface, instead of the normal heating and contraction that would take place as a result of conventional thermal expansion at slower rates, the heated layer will exert a pressure on adjacent material and a compressive shock wave will travel through the material. For example, when using a Q-switched ruby laser, acoustic transducers measured elastic stress waves induced in glass targets with a travelling compressive stress wave moving into the material from the irradiated surface which was reflected as a tensile wave at a free surface in the material. If the magnitude of these induced stresses becomes sufficiently large so that the shear stress of the material is exceeded, removal of material may take place by physical fracture. However, of more interest from the laser cleaning point of view is the proposition that the consequence of the rapid expansion and contraction of the treated surface could be the removal of a superficial deposit while at the same time the overall damage caused to the underlying substrate is negligible. This would mean that laser cleaning (for example of polluted layers from the surface of stone) could take place with the presence of an audible acoustic wave but in the absence of plasma formation or in a regime where plasma formation was not the main factor in determining the mechanism of cleaning. This could result in a mode of cleaning that is inherently less damaging to the substrate than the spallation mechanism. The evidence of this is given in the magnitude of the surface pressure that can be achieved as a result of the rapid thermal expansion and contraction effect.

White [23] modelling transient surface heating effects produced by repetitive laser pulses considered that temperature gradients both normal to and parallel to the surface are produced and result in thermal expansion which leads to strains in the body and stress waves which propagate away from the heated surface. The amplitude of the waves produced for a given absorbed power density depends on the elastic constraints applied to the heated surface. If this surface is unconstrained the stress amplitude may be relatively small but if the surface is constrained, for example by contact with another body, the stresses induced and the wave amplitude may be very large. Using a one dimensional surface heating model, it was deduced that for Type 304 stainless steel with an absorbed power density of $10^4$ W / $cm^2$ and a frequency of $10^5$ Hz, the peak temperature rise is 15.5 ˚C and that a surface stress of 3.8 x $10^7$ Pa (or 380 bar) would be produced for a constrained surface. This is 1.2 x $10^8$ times the photon pressure (see later). For an unconstrained surface, the stress would be only 17 times the photon pressure. The influence of constraining the surface has been utilised in laser based engineering processes such as laser shock hardening and laser percussion cladding [24 - 27]. Here, it is found that very large mechanical stresses can be applied, sufficient to mechanically deform the surface of metallic components but only if the surface is constrained by a film of liquid such as water or a plate of glass. In both cases, the laser used is transmissive of the surface film. It has been observed that laser cleaning in the presence of a water film is intensified compared to cleaning in the absence of such a film [28]. Fernelius[29] attributes discovery of a photoacoustical effect to Alexander Graham Bell in 1880 [30, 31] who observed that a periodically interrupted light beam impinging on a solid generates a sound wave in the gas above the solid. Under these conditions, the surface undergoes optical absorption and is heated by non radiative transitions. The periodic heating generates thermal waves and stress waves in the material which can be directly detected by attaching a transducer to the sample. Pulsed Q-switched ruby laser absorption in liquids was considered by Gournay [32]. Input fluence was 50 - 100 MW / $cm^2$ with a pulse length of 10 - 50 ns with a surface temperature rise of the order of only 10 degrees. Rates of change of temperature of 2 x $10^9$ deg / sec could be achieved. A 100 mW 30 ns pulse on water produced pressures of 40 atmospheres.

### 1.4 Evaporation pressure

A further mechanism which can produce high pressure pulses at an irradiated surface is the evaporation pressure. Aden et al [33] and Knight [34] discuss the generation of a laser induced shock wave as a result of the expansion of vapour away from a metal surface against the ambient gas. The concept is that there will be a region of compressed air between the advancing metal vapour and the ambient (uncompressed) air. The shock front would then be generated at the compressed air/ambient air interface. This mechanism would not require the absorption of laser energy in a plasma and would arise simply as a result of the high momentum of the evaporating material. High pressures are predicted in a model of this mechanism. Chan and Mazumder [35] state explicitly that for short, intense laser pulses, shock waves may be produced by the recoil pressure of rapid vaporisation of the material or by the interaction of the laser and the plasma, making it clear that these are two distinct processes. Ready [22] distinguishes recoil pressure pulses produced by evaporation and transient thermal heating effects as different mechanisms. Phipps et al [36] present an exhaustive account of experimental work on the pressure produced at metallic and non metallic targets under vacuum conditions where the intervention of an ambient gas (and hence the introduction of plasma blocking effects) is removed.

### 1.5 Photon pressure

There will be a small pressure exerted on a surface simply as a result of the momentum of the arriving photons. Although the mass of the photon is small, highly focused lasers are capable of providing a very high flux of photons [37]. The pressure delivered to the surface is small but perhaps capable of moving small surface objects. This mechanism has been considered in the case of the removal of sub micron particulates from microelectronic components. However, it is unlikely that sufficient force would be applied to the surface for art conservation purposes.

### 1.6 Ablation (bond breaking)

“Cold” ablation is an attractive mechanism in art conservation if it is the case that there is no (or little) attendant heating effect. Essentially, the energy, E, of a photon is dependent on its wavelength according to $E = h\nu$ (where h is Planck’s constant and ν is the wavelength). Hence the energy per photon of an excimer laser (4.9 eV) is some 40 times greater than that of a carbon dioxide laser (0.12 eV). Thus highly energetic ultraviolet wavelength lasers such as excimer, are capable of providing enough energy to directly break C-H bonds in organic materials. Since organic materials (including polymers) depend for their integrity on the presence of long chain molecules based on single, double or triple carbon-hydrogen bonds, chain scission by a photon with sufficient energy can lead to the production of short chains that can be easily removed by an air current or by light mechanical force. The effect is a known deleterious factor in commercial plastics where strong sunlight has been found to cause chain scission and hence mechanical degradation of plastics not containing UV stabilisers. In art conservation, the ablation effect produced by highly energetic photons has been applied to painting and rare manuscript conservation. It should be noted that the scission of double and triple carbon-hydrogen bonds requires photons of increasing energy and hence ultraviolet lasers of decreasing wavelength.

### 1.7 Angular Laser Cleaning

This technique [38] irradiates the surface at a glancing angle in contrast with conventional laser cleaning in which the laser beam is directed at a perpendicular angle of incidence to the target material, as shown in Figure 2. It has many advantages over conventional laser cleaning including a significant improvement in cleaning efficiency. It was found that, for the same laser input energy, the cleaned area irradiated at a glancing angle is up to 10 times larger than the typical laser cleaned area using normal incidence. Hence the speed at which contaminated areas are cleaned for the same incident laser energy is greatly increased. Moreover cleaning threshold fluence is reduced at glancing angles therefore reducing the risk of surface damage considerably in comparison with normal incidence laser cleaning.

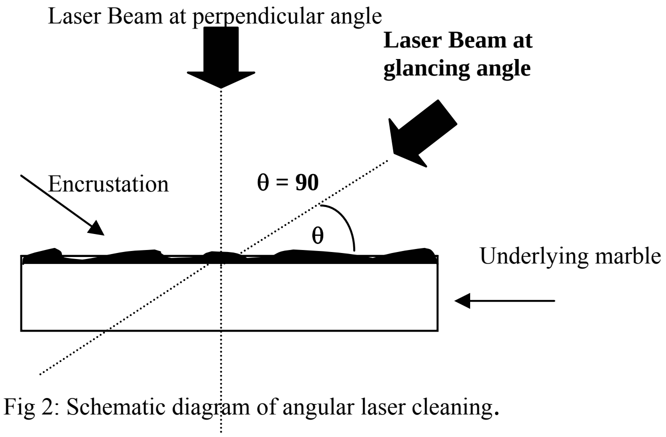

Fig 2: Schematic diagram of angular laser cleaning.

#### 1.7.1 The process mechanism

The action of a pulsed laser source on a spherical particle resting on a flat surface is shown in Figure 3 for the case of normal (a) and angular (b) incidence. Assume that the predominant cleaning mechanism is transient surface heating. If a laser pulse with a pulse length of $t_p$ is absorbed on the particle and the substrate, then a temperature rise ($\Delta T$) at the interface between the particle and the substrate surface is induced. The incident angle of the laser beam makes a difference in the laser absorption on the surfaces of the particle and the substrate and thus produces a different temperature rise at the interface. At the glancing angle of incidence (Figure 3 (b)), direct absorption at the interface between the particle and the substrate is possible. This absorption can be enhanced by multiple reflections and the increased absorption as a result of polarisation in the plane of laser incidence. However at the perpendicular angle, the temperature rise at the interface is restricted by absorption on the top surface of the particle and by the particle induced shadow on the substrate, as shown in Figure 3(a).

If it is assumed that most of the laser radiation is effectively absorbed at the interface at the glancing angle as shown in Figure 3 (b), the temperature rise at the interface can be simply estimated by a one-dimensional heat equation and be compared for the two different incident angles. For example, consider that the particle is copper and the laser used is a Q-switched frequency doubled Nd:YAG. The laser absorptivity for copper at the wavelength of 532 nm is 0.3, the pulse length ($t_p$) of the laser is 10 nsec and the laser fluence is 0.1 J/cm$^2$. If it is assumed that the particle size is 10 µm and that the laser absorptivity is increased to 0.8 at the glancing angle of incidence, the temperature rise for the perpendicular angle can be estimated to be approximately 10 $^o$C at the particle-substrate interface while the rise for the glancing angle case is 240 $^o$C at the interface.

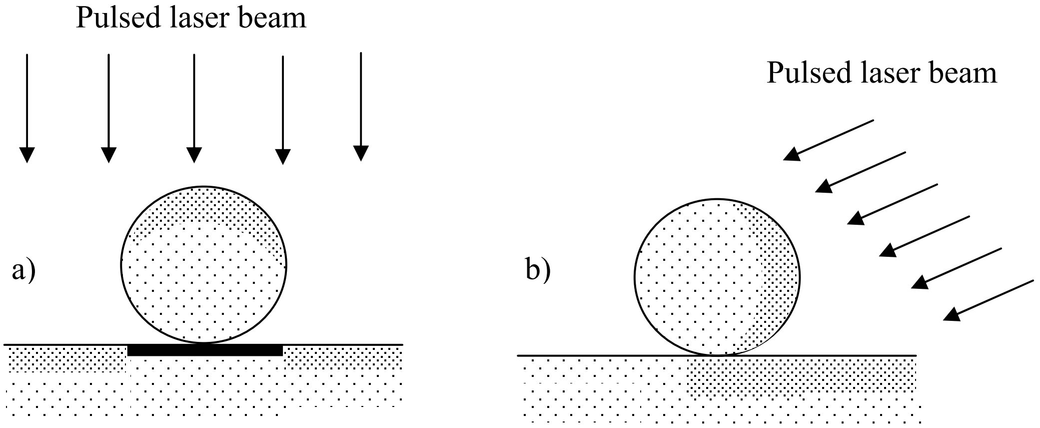

Fig. 3. Illustration of the laser absorption on the surfaces of the particle and the substrate for different laser incident angles (The density of "dots" indicates the amount of heating due to the laser absorption on the surfaces)

The normal expansion of the surface ($\Delta l$) due to the temperature rise ($\Delta T$) is given by:

$$\Delta l = \alpha \, \delta \, \Delta T, \qquad 1)$$

where $\alpha$ is the thermal expansion coefficient and $\delta$ is thermal diffusion length during the laser pulse. Inserting both the estimated temperature rises and the following typical numerical values for copper: $\alpha = 17.0 \times 10^{-6}\ K^{-1}$, $\delta = 2.1 \times 10^{-4}$ cm, the expansion amplitudes ($\Delta l$) are estimated as $3.6 \times 10^{-8}$ cm and $8.6 \times 10^{-7}$ cm for the perpendicular and the glancing angle respectively. If the expansion is achieved during the pulse duration of 10 nsec, the acceleration at the interface, a, resulting from the thermal expansion is approximately given by:

$$a = [\Delta l] / [\ t_p^2]. \qquad 2)$$

From (2) the accelerations at the interface are $3.6 \times 10^8$ cm/s$^2$ and $8.6 \times 10^9$ cm/s$^2$ for the perpendicular and the glancing angle respectively. Consequently, the thermo-elastic force, *F*, exerted at the interface is given by F = ma, where m is the mass of the copper particle, which can be calculated as $\rho \times V$: where $\rho$ (density) = 8.96 g/cm$^3$ ,and *V* (particle volume) = $5.24 \times 10^{-10}$ cm$^3$. The resulting thermo-elastic forces at the particle-substrate interface for perpendicular and glancing angles are 1.7 dyne and 40.4 dyne respectively. This points to the larger increase in efficiency of cleaning that results from the use of angular incidence. For the chosen conditions here the removal force is some 23 times larger than for perpendicular incidence. A fuller discussion of this model, together with experimental verification, is given elsewhere [38,39]

### 1.8. Laser Shock Cleaning

This technique [40] uses a plasma shock wave produced by a breakdown of air due to an intense laser pulse to remove the encrustations from the underlying marble substrate (Figure 4).

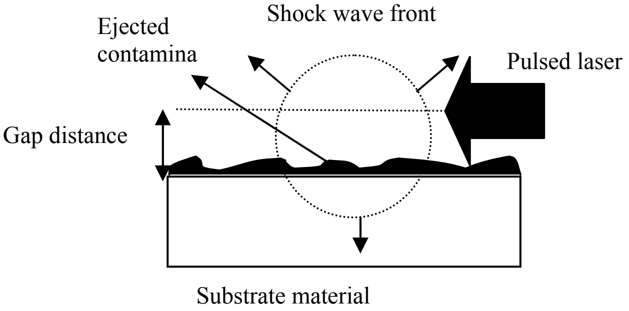

Fig 4: Schematic diagram of laser shock cleaning

The beam is directed parallel to the surface in order to avoid direct laser interaction with the target material and is tightly focused a few mms above the area to be cleaned. The power density of the beam at the focal point is around $10^{12}$ W/cm$^2$. The gaseous ambient constituents begin to break down and ionise and as a result a shock wave is produced which has an audible snapping sound. In air, the typical peak pressure of the shock front for a spherically expanding plasma is estimated to be the order of hundreds of MPa. However the precise value depends on the laser power density and the distance from the shock wave. This new approach has unique characteristics, as it is independent of physical properties of the contaminants (for example it does not depend on the absorptivity of the surface contaminant and hence may be useful in removing low absorptivity materials). Also, the risk of damage to the underlying substrate is much reduced as the incident beam does not come directly into contact with the workpiece. (However, the effect of the laser induced shock wave itself must be considered). Again, as with angular laser cleaning, an increased cleaning efficiency is observed in terms of the area cleaned for a given input of laser energy. It was found that the gap distance between the surface to be cleaned and the laser focus is critical in terms of successful cleaning as this distance alters the pressure of the shock wave striking the surface. In terms of practical application there may be limitation in the usefulness of the technique to the cleaning of flat surfaces.

## 2. Experimental Results and Discussion

Investigations were made in order to determine the effects of parametric variations (number of pulses, fluence, incident angle, gap distance) during the laser cleaning of marble using a Paragon Q-switched Nd:YAG laser operated at fundamental frequency (1064 nm). The artefact considered was marble with a dark encrustation that is typical of industrial pollution.

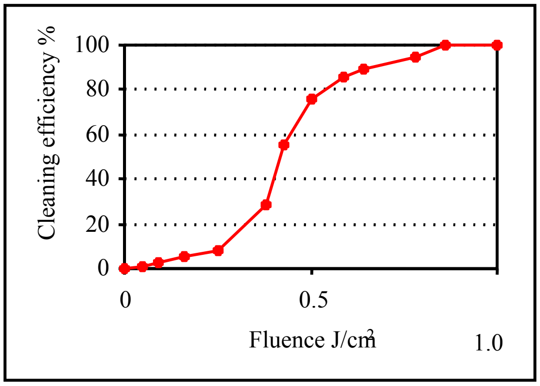

Fig 5: The cleaning efficiency of marble as a function of fuence using Nd:YAG laser at 1064 nm. 5 shots at a repetition rate of 0.63 Hz. Laser incident at 90 degrees.

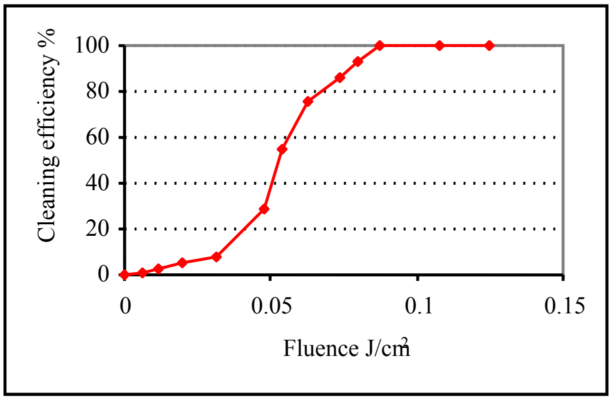

Fig 6: The cleaning efficiency of marble as a function of fluence using Nd:YAG laser at 1064 nm. 5 shots at a repetition rate of 0.63 Hz. Laser incident at 10 degrees.

Table 1 shows the irradiation conditions for normal incidence, angular incidence (10˚) and laser shock cleaning. The efficiency of cleaning was determined by optical greyscale monitoring (Optimus) of the surface before and after irradiation.

| **Mode of cleaning** | **Rep rate Hz** | **No. of shots** | **Laser Energy, J** | **Area cleaned $cm^2$** | **Optimum gap distance (mm)** |
|---|---|---|---|---|---|
| Conventional | 0.63 | 5 | ~ 1.0 | 1 | - |
| Angular | 0.63 | 5 | ~ 1.0 | 8 | - |
| Shock | 0.63 | 3 | ~ 2.0 | 3 | 2 |

Table 1: Comparison of the different modes of cleaning (Nd:YAG cleaning of marble)

Figures 5 and 6 show the threshold cleaning efficiency for removal of the encrustation by normal incidence cleaning and angular cleaning, respectively. The laser energy per pulse is similar in both cases (1 J) but in the angular cleaning case this laser energy is spread over a much larger area (8 $cm^2$) compared with the normal incidence case (1 $cm^2$), as shown in Table 1, and hence the threshold fluence for effective removal of the deposit is smaller by a factor of 8. This results in a significant increase in the cleaning rate (as shown in Figure 7).

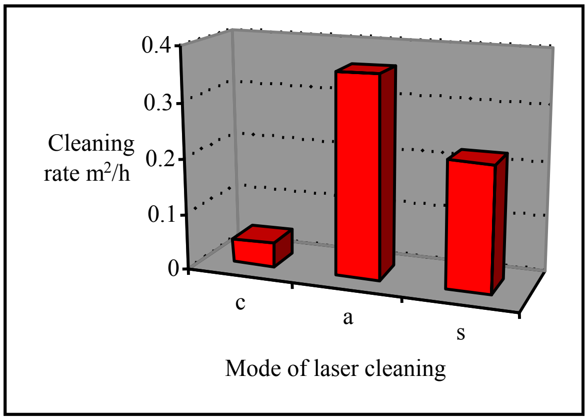

Fig 7: The cleaning rates for three different laser cleaning techniques; c-conventional(perpendicular irradiation), a-angular technique, s-shock technique.

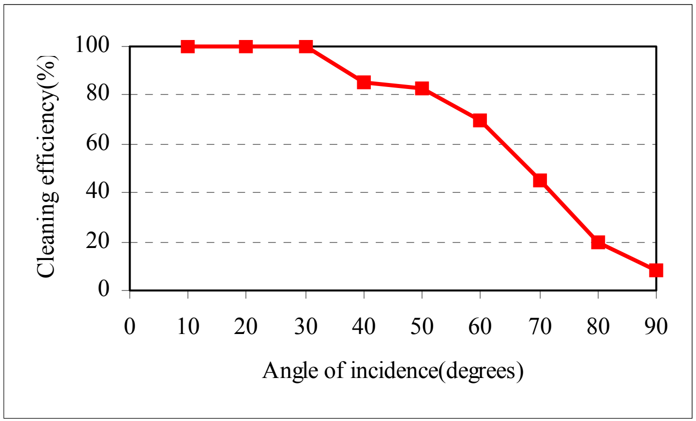

Fig 8. Variation of cleaning efficiency with angle of incidence for the laser cleaning of polluted marble

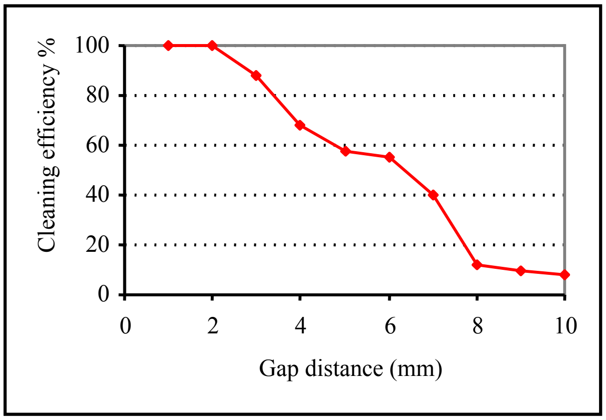

Fig 9: The cleaning efficiency of marble as a function of gap distance for laser shock cleaning using Nd:YAG laser at 1064 nm, 3 single shots parallel to surface at a repetition rate 0.63 Hz.

Figure 8 shows that for the laser cleaning of marble at a fluence of 0.15 $J.cm^{-2}$ the minimum angle of incidence at which the maximum benefit of angular cleaning is achieved is $30^0$.

For laser shock cleaning, it was found that the cleaning efficiency for a given laser energy was dependent on the distance between the laser focus position and the substrate – the gap distance - (Figure 9) with maximum efficiency reached at 2mm. At a laser energy of 2 J per pulse, an area of 3 $cm^2$ was cleaned in 3 shots, resulting in a cleaning rate that is intermediate between normal incidence cleaning and angular cleaning (Figure 7).

## CONCLUSIONS

1) A detailed review of mechanisms has shown that laser cleaning may be achieved by utilising a broad range of effects. Candidate removal methods include: selective vaporisation, spallation, transient surface heating, evaporation pressure and ablation (bond breaking).

2) For the case of transient surface heating, it has been shown that inclination of the incoming laser beam at an acute angle to the substrate (angular cleaning) can have a significant effect on cleaning efficiency. At an angle of incidence of $10^O$ the cleaning efficiency was increased by 8 times compared with perpendicular incidence (conventional) cleaning. Since the threshold fluence for cleaning was also lower in the angular cleaning case, a beneficial effect in minimising substrate damage would be expected. Further work is required to determine the effect of angular incidence cleaning while utilising the remaining laser cleaning mechanisms.

3) Laser shock cleaning offers a new technique for laser cleaning in which direct laser interaction with the substrate is minimised. It also offers improved cleaning efficiency over conventional incidence laser cleaning with a four fold improvement.

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