A REVIEW OF LASER TECHNIQUE APPLICATION IN CLEANING PROCESS OF POROUS CONSTRUCTION MATERIALS

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Abstract: This paper describes the review of laser cleaning methods for porous construction materials. The effects of laser radiation on substrate and the factors affecting the efficiency of graffiti removal are discussed. The laser cleaning (more precisely a degree of removability) depends on a large number of factors including surface roughness, porosity, cavity, moisture content, chemical/physical properties and thickness of graffiti, colour of graffiti, laser parameters such as energy, wavelength, duration and number of pulses, scanning speed (for continuous wave) and others. The most notable lasers already in use for laser cleaning are CO_2 laser, Nd:YAG laser, high power diode laser and a number of excimer laser systems. They have different properties and offer different advantages in practical applications. For example, excimer lasers can be used to remove varnish and unwanted paint layers successfully. Nd:YAG laser, which emits light of the wavelength of 1064 nm, can remove more material per pulse. On the other hand, high power diode laser is easy to use. Pop-out, cracking, cratering and/or glazing may occur in the case of laser cleaning, because substrate rapidly reaches high temperature when laser and substrate interact with each other. These problems are presented and discussed in this paper together with the advantages and disadvantages of these methods.

Keywords: cavity, graffiti, Laser cleaning, porous construction materials, surface roughness

1. INTRODUCTION

Over the last couple of decades graffiti has become a great problem particularly in the large agglomerations. It appears almost everywhere - on the external walls of buildings, girders and piers of bridges, underground passages, facilities in parks and roads. About 80% of graffiti is written with paint and marking pens on large walls, very often on historical objects (Matsui 2002). A considerable amount of money and time are spent annually on removing graffiti, City Councils have now begun to enforce regulations for keeping streets clean. According to these regulations, not only the person who wrote the graffiti is responsible for damage, but also the owner of the building on which the graffiti was written and unattended for a prolonged period of time. The traditional cleaning techniques are based on the use of a scalpel, abrasive dust, stream of fluid, or chemical agents. They may lead to the serious damage of the deeper layers of substrate.

Laser (Light Amplification by Simulated Emission of Radiation) cleaning is a good solution for removal of graffiti from surfaces, because the laser beam has unique characteristics than normal light, such as a single wave length (monochromaticity), is extremely parallel, it produces high power per unit area, coherence and it is highly directional. Furthermore, the laser cleaning process itself has several advantages, such as no mechanical contact, selectivity, localised action, no introduction of foreign contamination, less waste, flexibility, reliability and immediate feedback. However, laser cleaning process has some disadvantages as well, for example the capital cost is high and the laser cleaning should be done by the specialised/trained workers.

Although the method has been commercialised, there are no records of the comprehensive analysis of geometrical microstructure of cementitious composites and their effects on cleaning process. Highly developed surfaces of cement-based materials significantly complicate the mechanism of interaction between laser beam radiation and a base material. Even though it has been previously mentioned, no systematic approach has been adopted in analysing the process. It is also believed that some of the hydration products of Portland cement may be to some extent affected by a sudden increase in temperature. The presence of water in pore system adds even further complication to the process. This paper is a part of the larger project and aims to address only selected aspects of the laser cleaning. Special attention is paid to the effects of lasers and the geometrical microstructure of the cementitious composites.

2. EFFECTS OF LASERS

The selection of appropriate laser is the important role in the laser cleaning process. There are several parameters that should be considered for laser cleaning such as energy, wavelength, pulse duration and number of pulses, scanning speed (for continuous wave) etc. There are different types of lasers that can be used for laser cleaning such as CO_2 laser, Nd:YAG laser, high power diode laser and a number of excimer laser systems. The laser cleaning can occur photothermally, photochemically or both. In the photothermal process, the graffiti is removed by vaporization and it normally happens when the laser cleaning is done in the range of visible and infrared wavelengths. In the case of photochemical process, breaking of direct covalent bond of graffiti occurs. It happens when the laser cleaning is done in the range of ultraviolet wavelength (Cooper 1998).

2.1 Beam intensity

Beam intensity is the crucial parameter in laser cleaning process. If it is not correctly selected, it may damage the substrate. The beam intensity and their effects on the substrate and the graffiti are presented in figure 1 below:

<table>
<tr><td>Beam intensity</td><td colspan="4" align="center">Increasing</td></tr>
<tr><td>Effects on the graffiti and substrate</td><td>No damage to material</td><td>Local damage and ablation of surface material</td><td>Melting</td><td>Ablation of material by ‘explosive vaporization’</td></tr>
<tr><td>Temperature rise</td><td colspan="4" align="center">Increasing</td></tr>
</table>

Figure 1: Effects of power density of Q-switched laser radiation (visible and infrared wavelengths) on the paint and the substrate (Cooper 1998)

The removal time of graffiti also changes according to the beam intensity. Following equation shows the relationship between paint removal time and beam intensity:

$$\Delta t = CI^{-n} \tag{1}$$

Where, Δt (sec) is the total irradiation time, I (W/cm^2) is the beam intensity and C and n are the positive constants for particular type of laser, paint thickness, paint colour and paint type (Liu 1995).

2.2 Wavelength of laser vs. colour of graffiti

The selection of wavelength of cleaning laser depends on the colour of graffiti and the type of graffiti. When wavelength of graffiti colour is similar to the wavelength of cleaning laser, absorption is low. Thus the wavelength of cleaning laser should not be same as wavelength of graffiti colour. Generally shorter wavelength is better than the longer wavelength because absorption coefficient decreases bit by bit when the wavelength of laser increases. Shorter wavelength (third harmonic) of Nd:YAG is much better than longer wavelength (fundamental wavelength) of Nd:YAG (Liu 1995, Costel 2003). The wavelengths of each laser types are given below (see Figure 2).

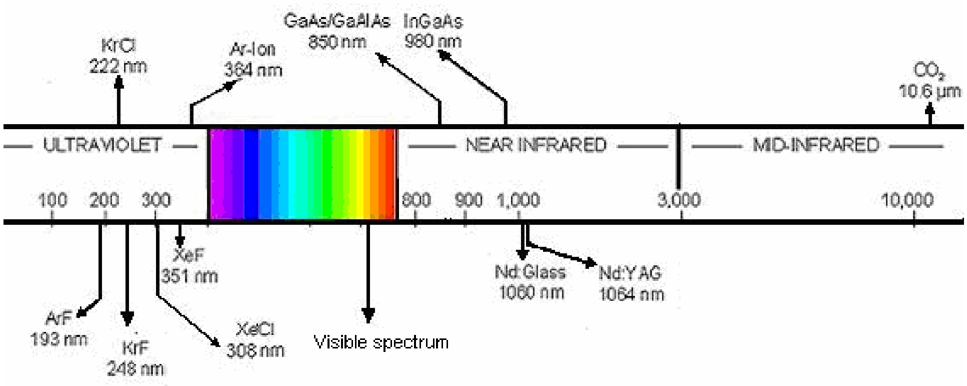

Figure 2: Wavelength of the lasers

2.3 Beam Area

Beam size is one of the factors that influence cleaning efficiency and time of cleaning. Relationship between the total area of paint removable and the beam area can be shown by the following equation:

$$A_T = \frac{1}{C}\left(\frac{E_0^{\,n}}{\delta t_p^{\,n-1}}\right) A_b^{\,1-n} \tag{2}$$

Where, A_T is the total area of paint that can be removed, A_b is the beam area, E_0 is the total laser energy and δt_p is the pulse width. Assuming that pulse width (δt_p) can be scanned over a paint sample (Liu 1995). A smaller beam size is normally good for laser cleaning process, because of the high removal rate and the less cleaning time. However, if the laser beam area is too small, it may damage the surface. Thus the beam size should be selected carefully.

2.4 Pulse duration

Pulse duration is the time it takes for the laser to emit one pulse (see figure 3). In the case of long-pulse lasers and continuous lasers, the removal of paint is done by vaporization. At the same time, ablation of paint material occurs in the case of high power short-pulse lasers, by acoustic shock waves created by the absorption of high-intensity laser energy (Liu 1995). A higher removal rate can be achieved in the case of short pulses for a fixed amount of laser energy.

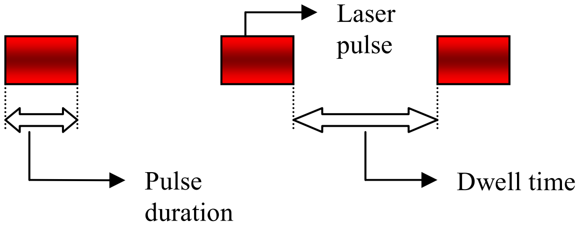

Figure 3: Illustration of laser pulses

If the pulse duration is too short, the cleaning is not efficient, at the same time if pulse duration is too long, substrate is affected by heat. Thus appropriate pulse duration should be selected (Crivella).

2.5 Pulse repetition rate

Pulse repetition is the number of pulses per second. If dwell time is too short (see figure 3), the dust from the graffiti and the laser pulse interfere with each other. Hence the laser pulses do not reach the target (see figure 4). If the pulse repetition rate is too long, the cleaning takes more time. Therefore pulse repetition rate should be selected as appropriate (Crivella).

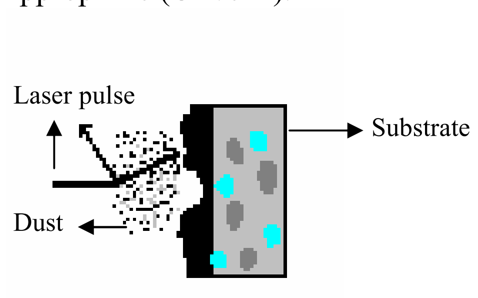

Figure 4: Laser and dust from the graffiti interaction

2.6 Number of pulses and scanning speed

Generally numbers of pulses are decided base on the thickness of the graffiti. If the thickness is high, the number of pulses required for cleaning graffiti is high for a given fluence. The relationship between number of pulses required for removing paint, pulse width and fluence is given by following equation:

$$t_b = N\delta t_p \tag{3}$$

$$I_b \delta t_p = F \tag{4}$$

$$N = C\left(\delta t_p\right)^{n-1}\left(F^{-n}\right) \tag{5}$$

Where, N is the number of pulses, t_b is the irradiation time required for removal of paint from the beam area (A_b) and F is the fluence (Liu 1995). When fluence increases the number of pulses required for cleaning decrease. Thus the time required for laser cleaning become less if the fluence of laser is high. However, the irradiation with low fluence with large number of pluses is better because it does not damage the surface (Matsui 2002). In the case of continuous laser, the scanning speed influences the efficiency of the laser cleaning process and the time of cleaning. Under high speed and low speed scanning by laser, the surface might not be cleaned and get damage respectively. Therefore scanning speed should be selected as appropriate.

2.7 Angle of incidence of the laser beam

There are two different way of laser cleaning other than conventional perpendicular laser cleaning, i.e. angular laser cleaning and shock laser cleaning. The angular laser cleaning means that laser is applied at a glancing angle, and the shock laser cleaning means that plasma shock wave is produced by breakdown of air near the cleaning surface; because of the high power pulse laser is used for cleaning, where the laser beam is parallel and close to the surface. These two methods have several advantages over the conventional perpendicular laser cleaning, such as cleaning area is high for same laser input energy, cleaning speed is high, cleaning threshold fluence is less and the risk of damaging the surface is less (Watkins 2003).

3. EFFECTS OF GRAFFITI

Basically, the type of graffiti to be cleaned influences the selection of laser parameter for cleaning. There are different types of graffiti materials such as spray paints, marking pens, lipsticks, adhesive label and physical scratching of surface. Each graffiti material has unique colour, thickness, physical properties and chemical properties. These factors affect the laser cleaning process.

3.1 Graffiti thickness

The thickness of graffiti mainly influences the cleaning time. More time is needed for thick graffiti. The relationship between removal depth by photothermal process and other parameters is given by the following equation:

$$H_V = \frac{\Delta t A P_d}{\rho\left(CT_v + L_f + L_v\right)} \tag{6}$$

Where, Δt (sec) is the beam/material interaction time, A is the material absorptivity, P_d (W/cm^2) is the laser power density, H_v (cm) is the depth of vaporisation, ρ (g/cm^3) is the materials density ,C (J/gK) is the specific heat of material, T_V (^{o}C) is the vaporisation temperature, L_f (J/g) is the latent heat of fusion, L_v (J/g) is the latent heat of vaporisation. The assumptions are the thermal losses by conduction and glazing of the remaining surface are neglected. In the case of cementitious materials and bricks, thermal conduction is low. Therefore the above assumptions are justifiable (Li 1994).

$$H_P = \frac{1}{\alpha} \ln \frac{F}{F_T} \tag{7}$$

Where, H_P (cm) is the removal depth per pulse by photochemical process, F (Jcm^{-2}) is the incident fluence, F_T (Jcm^{-2}) is the threshold fluence and α is the extinction (Schmidt 2003). In the above two processes, the removal time is influenced by the paint thickness.

3.2 Chemical/physical properties of paint

The chemical and physical properties of paint influence the selection of laser parameters for laser cleaning. In the case of photochemical ablation, laser cleaning is done by direct bond breaking. The energy should be fair enough to break the covalent bond of paints (see table 1). The photothermal ablation happens by vaporization. Therefore laser should provide enough energy to increase the temperature of the paint to evaporate (Cooper 1998).

Table 1: The average covalent bond energies (Cooper 1998)

Type of covalent bond	bond energy(J)
C-C	$5.76*10^{-19}$
C-O	$5.92*10^{-19}$
C-H	$6.88*10^{-19}$
O-H	$7.68*10^{-19}$
C=C	$10.24*10^{-19}$

4. EFFECTS OF SUBSTRATE

The effects of substrate properties such as surface roughness, cavity, porosity and moisture content of the substrate are regarded as very important surface parameter for laser cleaning (Matsui 2002, Rozniakowski 2001).

4.1 Surface roughness

The surface roughness is defined as the vertical variation over a measured distance. It can be defined by different ways such as average roughness (*Ra*), root mean square roughness (*Rq*) highest peak in the roughness profile (*Rp*), the depth of the deepest valley in the roughness profile (*Rv*) etc. In between these parameters, *Rq* is more related to the optical quality of a surface. Therefore the laser cleaning is believed to be related to *Rq* value more than the other parameters. Furthermore *Rv* may also influence the purity of the laser cleaning. If *Rv* is high, the paint can penetrate more. Thus laser cleaning may be difficult.

$$Ra = \frac{1}{a} \int_{x=0}^{a} |f(x)| dx \tag{8}$$

Where, *f(x)* is the surface height measured from the mean line and '*a*' is the total distance that surface roughness is considered. The root mean square roughness (RMS) is:

$$Rq = \left(\frac{1}{a} \int_{x=0}^{a} f^2(x)dx \right)^{1/2} \tag{9}$$

When average roughness increases (more than wave length of laser), absorption increases, because of the multiple reflections of laser. In the case of smooth surface, where average roughness is less than the wavelength of laser, absorptivity is fairly low. Furthermore adhesion increases with the roughness (*Ra*) (Mellali 1995). The laser cleaning process is influenced by not only adhesion of the graffiti but also the absorption of laser for the particular laser power. When adhesion increases, laser cleaning will be difficult. At the same time, laser cleaning will be easy when absorption increases for constant laser power. Both events happen at the same time in opposite directions. Therefore the effect of surface roughness on the laser cleaning might be a combination of the above two events.

In the case of carter formation and pop-outs, the surface roughness seems to be increased when compare to the initial roughness of cementitious material. At the same time, the surface roughness of the substrate decreases in glazing (Lawrence 2001). Pit-holes (little holes that appear on the surface of cementitious composites) may affect the surface roughness of the substrate and the laser cleaning process as well (see figure 5). If there are finer pit-holes, laser cleaning would be difficult.

Figure 5: Mortar surface

4.2 Cavity

Cavity is defined as a ratio of the lateral surface of the niche to the surface of the entrance to the niche. Cavity is measured as a ratio of real length (L_r) of the profile to the geometrical length (L_o) of the examined profile (see figure 6) (Wieloch 2004).

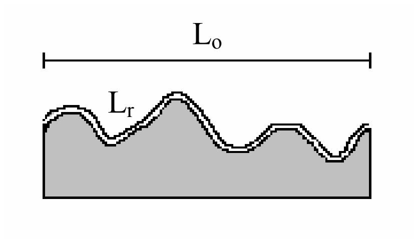

Figure 6: The cross section of the surface

The cavity is high means that it has more surface area per projected surface area. When the cavity is high, there are more surfaces to be cleaned, and sometimes more difficult to clean as well (see figure 7).

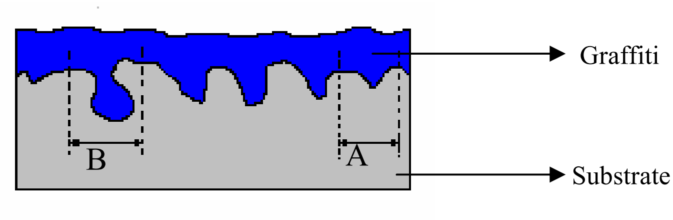

Figure 7: The profile of painted substrate. The region 'B' has a narrow opening (cavity is high). Therefore, the removal of graffiti is difficult. The region 'A' has a wide opening (cavity is low). Therefore, the removal of graffiti is easy.

4.3 Porosity and moisture contents

The porosity and the moisture contents work together and affect the laser cleaning. When high energy is applied to wet mortar with low porosity (low water cement ratio), pop-out occur. In the case of absolutely dry mortar with low water cement ratio, hair cracks occur in high energy irradiation. No damages occur in mortar specimens with high porosity (high water cement ratio) and low energy. Therefore graffiti removal should be done on dry surfaces if it is possible (Matsui 2002).

5. EFFECTS ON THE SUBSTRATE

Pop-out, cracking, cratering and/or glazing may occur on the substrate in the case of laser cleaning, because substrate rapidly reaches high temperature when the laser is applied. If concrete is heated up, the following physical and chemical changes occur:

Table 2: The temperature regions that damages occur (Schmidt 2003)

Temperature range	Effect
Up to 400 ^oC	Loss of physically bond water from pores and gel
400-540 ^oC	Dehydration of $Ca(OH)_2$
570-573 ^oC	Conversion of quartz from α to β phase
600-700 ^oC and above	Decomposition of C-S-H*
800 ^oC and above	Decarbonation of $CaCO_3$
1150-1200 ^oC and above	Melting

*C-S-H means amorphous calcium silicate hydrates

There are no comprehensive analyses of the effect of temperature on the cementitious materials due to laser cleaning. However, a lot of researches have been done on the effect of temperature rise on cementitious material within some considerable time (eg 20 minutes) (see table 2). In the case of laser cleaning, temperature rise occurs within a short time (ns) on the substrate. Sometimes it does not affect the deep part of the substrate, especially if laser parameters are selected correctly. Thermal conductivity of cementitious material is low. Thus when temperature rises on the surface for short time, heat may not affect the deep part of cementitious material.

OPC concrete contains 70% of $CaO-SiO_2-(H_2O)$ gel, 20% of well crystallised $Ca(OH)_2$, ettringite ($CaO.Al_2O_3.SiO_2.12(H_2O)$), calcium aluminate monosulfate hydrated ($4CaO.Al_2O_3.13(H_2O)$) and some minor phases. Dehydration start when the concrete surface is heated for considerable time and water will lose at 200 ^oC. The break down of hydrated chemical bond occurs at around 550 ^oC and it completely breaks down at 800-900 ^oC. However, further heating at around 1600 ^oC creates stable ceramic bond (glazing), such as $CaO.SiO_2$, 2CaO.SiO2, anorthite ($CaO.Al_2O_3.2SiO_2$), and rankinite ($3CaO.2SiO_2$) (Li 1994).

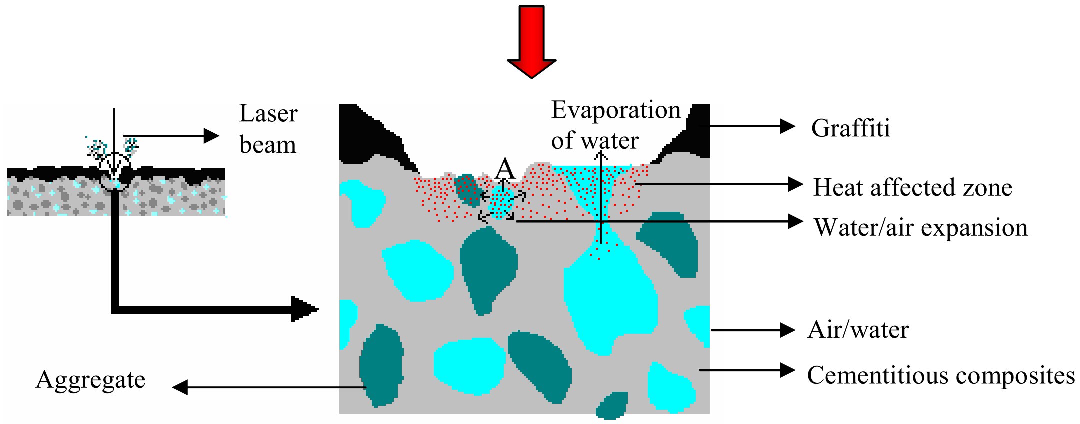

Figure 8: Effect of laser cleaning on the porous material. The point 'A' is the potential point that pop-out may occur

In the heat-affected zone, water/air in the pores absorbs the heat and try to expand. As a result out ward pressure build up inside the pores. If there are pores, which are exposing to atmosphere, water/air dissipates the pressure through those pores. Otherwise water/air inside the pores tries to break the weak section. When breakage happens - so called pop-out, all the pressure dissipates (see figure 8).Aggregates and cementitious composites have a different thermal expansion coefficient. Thus cracks may develop in between cementitious composites and the aggregates in the heat-affected zone.

6. FINAL REMARKS

The advantages and the disadvantages of each type of lasers depend on the laser parameters selected, the type of graffiti to be removed and the type of substrate to be cleaned. However, there are some unique advantages and disadvantages of these lasers. The Q-switched Nd:YAG laser is most effective and extremely reliable. It has a higher efficiency than the excimer lasers (Liu 1995) but controllability is less than the excimer lasers. All colors of the paints can be removed by CO_2 laser and the absorption of the CO_2 laser is high in ceramics and polymer (LI 1994). The high power diode laser is easy to operate, because the size of the laser is small and the excellent control of removal depth. The excimer lasers are used for removal of varnish and unwanted paints. These lasers have a higher degree of controllability than other lasers, but redeposition of the graffiti and low removal rates are the problem of these lasers (Schmidt 1999).

Although a lot of researches were carried out on laser cleaning, there are no records of the systematic analysis of geometrical microstructure of cementitious composites and their effect on the laser cleaning process. The effects of the surface roughness, the cavity, the pit-hole, the porosity and the moisture content on the laser cleaning process will be tested and analyzed in comprehensive manner in near future.

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