Laser cleaning of stones

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Captions will be soon available in english.

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History of laser cleaning: From the first experiments to the validation of the method

The word "laser" is actually an acronym for light amplification by the stimulated emission of radiation, a technique that was developed in the mid-20th century. In 1917, Albert Einstein identified a phenomenon he called "stimulated emission of radiation", a concept which eventually led to the development of the laser. The appearance of the first operating laser dates to 1959, built by Theodore Maiman, an American physicist. In spite of fruitful experiments in the 1970s, especially thanks to the pioneering work of John Asmus who was the first to test the method and publish encouraging results [1], it was not until the late 1980s that heritage conservation scientists would delve into this question and consider the development of a laser specifically designed for the cleaning of stone.

The Laboratoire de Recherche des Monuments Historiques (LRMH) in Champs-sur-Marne was a leader in this field in France and in Europe. Already in 1987, one of its engineers joined forces with a manufacturer (B.M. Industries, based in Evry) with the aim of developing a mobile laser unit to be used on heritage sites, able to clean stone adequately and that would be usable on scaffolding and in workshops for a reasonable cost. Different types of lasers were tested on stone samples brought back to the laboratory. One type of laser and a specific wavelength were quickly selected as the most effective, reliable and least damaging to stone [2]. It would be several years before a prototype (NL 00) could be manufactured for use on site and then tested on stone samples from various monuments brought back to the laboratory for experimentation and analysis, in order to assess its cleaning capacity [3]. At the same time, several studies were launched to compare the results of laser cleaning with those obtained using other methods, such as micro-sandblasting or the application of compresses [4, 5]. These experiments demonstrated that the performance of laser cleaning could exceed that of traditional methods. Based on these encouraging results, laser cleaning was adopted by a first major restoration project in 1993 at the Amiens cathedral [6], a UNESCO World Heritage site. The first compact, reliable and mobile machine for use on heritage sites was marketed under the name NL 101 by B.M. Industries. British physicists and conservators, who had also been developing a stone cleaning laser, carried out their first tests in 1992 [7]. A European consortium bringing together the laser manufacturer Quantel, several fieldstone quarrying and masonry firms, and laboratories in France and Portugal successfully initiated a project which resulted in the construction of several machines, while a university dissertation furthered our understanding of phenomena and mechanisms involved in stone cleaning [8].

Today, many prestigious sculpted portals of major cathedrals, churches and other monuments have been cleaned using one or more types of lasers [9] and we can consider that in France, beginning in about 1995, laser cleaning definitively joined the arsenal of procedures used by sculpture restorers. In Heraklion on the Greek island of Crete, the first international conference on the use of lasers in the conservation of art works was held in 1995, now known by its acronym LACONA (LAsers in the CONservation of Artworks). Since then, this event has been organised every other year in a different country. The next conference, LACONA VII, will be held from 17 to 21 September 2007 in Madrid (Spain).

Currently, two families of cleaning lasers are used in France and some ten different lasers are available in Europe.

Principle of the laser

The term "laser" is ambiguous since we use it to describe both the mechanism, the source used to create and emit this special kind of light, and to refer to the beam of radiation itself.

Lasers are based on the principle of the amplification of light through the stimulation of radiation or optical pumping. An incoming photon (with energy = E2 – E1) stimulates an excited ion (with an excited state of E2 and a ground state of E1) to undergo a transition from the excited state (which is unstable) to the ground state, emitting a new photon with energy equal to the difference between E2 and E1, having the same wavelength as and in phase with the incoming photon (dual nature of light as wave and particle) that will propagate in the same direction as the initial incident radiation (Figure 1).

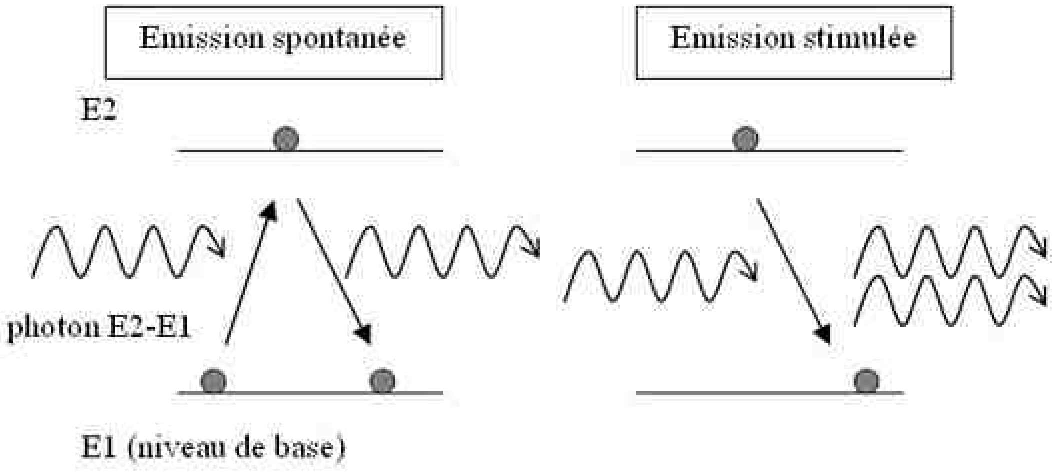

Figure 1: Schematic representation of spontaneous emission and stimulated emission (laser source) for a two-level atom with a ground state and an excited state.

These two photons will then excite two other ions and so on, resulting in a larger number of photons or waves of the same wavelength propagating in phase in the same direction between the two mirrors (one of which is partially reflective) positioned in the resonant cavity of the laser. The sum of these stimulated emissions generates what is known as "coherent" light (a beam of light whose photons all have the same optical properties: wavelength, phase and direction) of very high energy, very different from "natural" light, such as that emitted by a light bulb (heated filament), which is diffused or scattered, of low energy and incoherent since it consists of a large number of different waves propagating in every direction. Due to the principle behind its generation, laser light has very specific properties: it is monochromatic (a single wavelength) and coherent (all waves are in phase in time and space). This type of light is also very directional, high in energy and highly collimated (nearly parallel rays).

These properties of laser light are used for various applications (topographic surveys, welding, etching, sight lines, microsurgery, reading of bar codes, etc.). Like all other light, that produced by a laser is an electromagnetic wave, but it differs by being monochromatic. Each laser is characterised by a specific wavelength. Lasers used to clean sculptures emit in the near infrared spectrum, beyond that of visible light, exactly at a wavelength of 1064 nanometres. Other lasers intended for different applications emit in the ultraviolet range or in the visible spectrum.

The laser machine

The machine used for stone cleaning is a robust Q-Switched Nd:YAG laser. This seemingly complex terminology is easy to explain. The laser source is a mineral rod composed of yttrium aluminium garnet. This solid-state crystal matrix is doped with neodymium ions in several possible valence states. It is these ions which, once excited by the beam of a flash lamp (filled with xenon, flash duration of about one millisecond), will undergo a transition to a stable state at several excitation levels (optical pumping) and will generate a set of coherent monochromatic waves by decaying cyclically to more stable states. The cleaning laser is not a low energy continuous emission laser like those used for sight lines, but is instead a high energy switched pulse laser: the photons (or waves) emitted in the pumping chamber are stored until their intensity reaches a high threshold then released from the pumping chamber in the form of very rapid pulses of about 6 to 15 nanoseconds (10^{-9} seconds). The energy generated by each pulse is very high, about 10 joules, and the power output amounts to several hundred thousand watts. Depending on the machine used, the laser may be capable of releasing from 1 to 15, 20, 30 or 60 pulses per second. This high firing frequency allows the laser to be used as a continuous beam that can be moved along the surface to be cleaned.

A few figures:

For a cleaning laser with a wavelength of 1064 nm and the following average conditions:

- energy of a single pulse E = 1 joule
- pulse duration T = 10 nanoseconds (10×10^{-9} seconds)
- firing frequency y = 20 hertz

We obtain the following parameters:

- Peak power $P_{peak} = E/T = 1/10 \times 10^{-9} = 108$ W or 100 MW

- Average power $P_{avg} = E \times y = 1 \times 20 = 20$ W
- Fluence, or energy density, depends on the spot diameter. For a beam with spot diameter s = 1 cm^2, the fluence $F = E/s = 1/1 = 1$ J/cm^2. If we enlarge the spot diameter to 2 cm^2, the fluence decreases (F = 0.5 J/cm^2).
- for a spot diameter of 1 cm^2, luminance = $P_{peak}/s = 100/1 = 100$ MW/cm^2

The three main components of a cleaning laser are the generator, the cooling system and the laser unit (which may include several crystal rods and flash lamps). In practice, these components are presented as two or three mobile units, since the laser unit and the cooling system or the generator may be grouped together on the same frame or cart. Depending on the model and its output power, the total weight of the machine may range from 100 to more than 400 kg. Lastly, two types of models are available from different manufacturers, with the emitted laser beam directed either along an articulated arm to a handheld touch trigger probe or via a fibre optic delivery system. Depending on the type of lens placed at the end of the handheld probe, the laser beam may be parallel (collimated), convergent or divergent, with varying focal lengths.

There are three possible adjustments the operator may use to optimise the cleaning:

- Potentiometer: knob used to adjust the energy per pulse.
- Frequency divider: knob used to adjust the firing frequency.
- Lastly, for a given energy per pulse, it is possible to modify the energy density by moving the handheld probe forward or backward. Thus in the schematic diagram shown in Figure 2, with a convergent beam and a long focal length, the spot diameter increases when one reduces the working distance by bringing the probe closer to the surface to be cleaned. The pulse energy is then distributed over a larger area and the energy density (fluence) decreases. With the more powerful machines, the spot diameter of the beam may be as large as 15 or 20 mm, meaning that surfaces may be cleaned much more quickly [10].

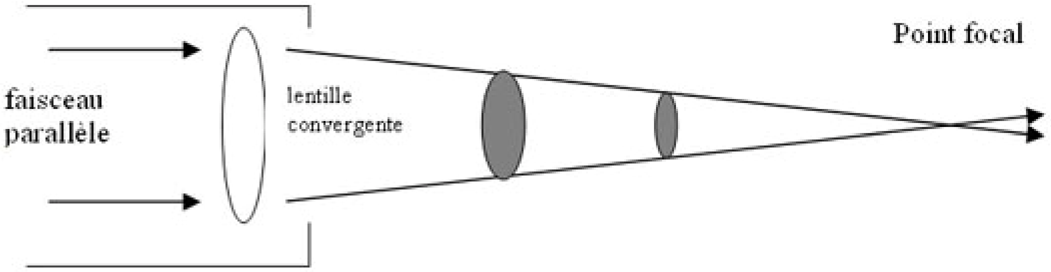

Figure 2: Schematic diagram of a laser beam focused using a convergent lens placed at the end of the probe. The spot diameter increases when the lens is brought closer to the surface, resulting in a decrease in energy density. Conversely, by increasing the working distance, we move closer to the focal point, the spot diameter decreases to a minimum and the energy density increases.

Principle of laser cleaning: Interactions between light and matter

The soiled and grimy stone is covered with a deposit consisting of various microparticles (fly ash and fine soot produced by automobiles or industrial processes, pollens, spores, windborne seeds) cemented by gypsum. These black encrustations are a familiar site in polluted industrial or urban areas. During the cleaning process, the high energy laser beam is significantly absorbed by these dark-coloured surface stains (whereas the stone itself, generally light-coloured, white to yellow, tends to reflect the incident radiation). The mechanisms involved, which have a total duration of only a few billionths of a second, are not fully known. However, we do know that the removal of the stains (photoablation) results from a combination of thermal and mechanical interactions between the absorbed radiation and the surface treated [7].

Thermal interaction

This interaction causes a rapid, very localised and very brief rise in temperature on the surface of the material which leads to melting and vaporisation and finally results in the formation of plasma (neutral ionised gas) with a temperature as high as several thousand degrees. Physical models and attempts at measurement have indicated that there is not any significant transfer of heat to the stone. No high-temperature mineral phase transition has been observed on the cleaned surface. It has been demonstrated for the cleaning of plaster that gypsum, its main component, which is stable up to a temperature of about 100°C, does not undergo any conversion into hemihydrate or anhydrite.

Mechanical interaction

The laser-induced formation of plasma, followed by its dynamic expansion, generate mechanical shock waves and sound waves that propagate through the material, break it down and cause the dispersal of particles of various sizes, thus accompanied by a characteristic crackling noise.

Under optimal operating conditions for cleaning lasers, the extent of thermal versus mechanical effects depends on several factors, such as the pulse duration, the nature of the materials, and the presence of water.

It is now understood that the different properties (optical, mechanical, thermal, etc.) of the stains and the stone are determining factors for the effectiveness and quality of the ablation process. Above a specific threshold (called the ablation threshold), laser adjustments used to eliminate stains are ineffective on the stone itself and on patinas, which are much more compact and reflective. We thus refer to the selective and self-limiting nature of laser cleaning. Nevertheless, in some cases, for instance where the elimination of earlier, light-coloured and dense coatings is required, the conditions for the self-limiting cleaning regime are not met and it will be the mission of the restorer, owing to his or her expertise and dexterity, to remove the undesirable layer without altering the stone underneath, as is often performed when using other more traditional cleaning techniques (micro-sandblasting, application of compresses, etc.).

Lastly, the mechanical effects are intensified if the stains contain water. The explosive vaporisation of water induced by the laser increases the particle dispersal rate. It is for this reason that restorers usually moisten the stains by spraying them with water while using a cleaning laser.

Advantages and limitations of laser cleaning

Lasers use only radiant energy, without water (steam cleaning, compresses), chemicals (alkalis, acids, sequestering agents, etc.), abrasive particles (micro-abrasion) or pressure. On fragile, chipped, powdery, disintegrating surfaces, it is therefore possible to clean hardened black encrustations without the risk of physical damage to the stone (Photo 1).

Photo 1:
Laser cleaning of sculpture (statutory from the north portal of the Saint-Michel Basilica in Bordeaux) covered with a black, hardened encrustation but whose outermost layer had become very brittle and fragile due to alteration. The fine, raised flakes of stone are especially worth noting. The laser allows for superior quality cleaning, respecting the sculpted surface without the need to strengthen the surface beforehand. (Photos: L.R.M.H.).

In the past, for this type of restoration project, prior reinforcement of the stone was an inescapable preliminary to traditional cleaning. But this operation, which involves injecting a binding agent such as ethyl silicate underneath and around the area to be cleaned, is very delicate, fastidious and time-consuming. Furthermore, laser cleaning is a very selective method, able to eliminate the finest of layers, provided it is sufficiently different from the substrate surface. The result may be examined as the operation proceeds and the cleaning may be interrupted at any time.

These advantages make the laser the ideal choice for the cleaning of sculptures that have become brittle with alteration. Laser cleaning is superior in many ways but it is also a slow and costly process that cannot be applied as such to all stone facing. For sculpted portals, where the surfaces to be cleaned are sizable, it is not uncommon for restoration workshops to use several (as many as four) lasers together.

Laser cleaning has not replaced all other methods, but it has taken pride of place among the panoply of techniques available to sculpture restorers, alongside micro-sandblasting, compresses, gentle brushing and the use of hand tools. The type of stains, the presence of polychrome traces or of previously cleaned layers may also influence the definitive choice [11]. Comparative tests on sample regions (Photo 2) are recommended [12]. In addition, laser cleaning is not able to remove organic layers (moss, lichen, algae), dust deposits on furniture and impregnated spots (such as graffiti ink), which would respectively be handled using a biocide, brushing combined with vacuuming and the application of compresses soaked in solvents.

Photo 2: Test of laser cleaning on a sculpted arch stone as part of the preliminary study for the restoration of the north portal of the Saint-Michel Basilica in Bordeaux (Photo: T. Vieweger).

Already in the early days of its use, some critics noted the yellowing of stone caused by laser cleaning. Further experience has seemed to confirm this yellowing, the source of which has yet to be determined. However, the patinae of ancient stone under the black encrustations are usually yellow or ochre coloured. Laser cleaning only serves to intensify a pre-existing yellow colour that corresponds to underlying patinae whose preservation is an indication of the quality of the cleaning performed. Nevertheless, some architects have developed complex cleaning procedures associating laser and compresses with the aim of partially eliminating this characteristic yellow tinge (Photo 3). The laser is thus used due to its superior performance, its exceptional preservation of the stone’s epidermis, while the application of compresses attenuates the yellowing [9]. Experiments have also been performed, demonstrating that it is possible to use laser cleaning without an yellowing effect by combining simultaneous emission of basic frequency in the near infrared spectrum at 1064 nm with the third harmonic in the ultraviolet range at 355 nm [13].

Photo 3: Attenuation of the yellow tinge caused by laser cleaning, through the application of water compresses in the lower part of the image; restoration of the central portal of the western facade of Notre-Dame Cathedral in Paris (Photo: M. Labouré).

The laser would be the ideal tool to clean polychromes and wall paintings, if only it did not modify the colours of many ancient pigments. Research efforts to deepen our understanding of the mechanisms of these discolourations are under way in several laboratories, with the hope one day of discovering a solution to this problem. Different lasers have been tested, as have shorter pulse durations, in the region of a femtosecond (10^{-15} seconds). In the meantime, at the very least it is essential to perform tests on small areas before beginning to use a laser to clean an entire paint layer.

Laser cleaning in practice

Costs and installations required for laser cleaning

The use of a laser involves specific costs in connection with:

- assembling and dismantling a wooden structure
- procurement and installation of a black tarpaulin
- delivery, setup and removal of lasers

- maintenance of lasers (as sensitive electronic and optical equipment, they require regular maintenance in addition to services performed by a laser engineer, including the preparation for return shipping of machines)
- recalibration of lasers after completion of work

The requirements in relation to scaffolding are as follows: black weatherstripping of windows and openings, 1.50 m platform with plywood covering, tarpaulin over the scaffolding, 180 kg lifting capacity, 1.50 m x 1.50 m crane tower with access to all levels of the scaffolding, EDF single and three phase 25 kWh.

Lastly, as is also the case for most of the other techniques, laser cleaning is not possible in very cold weather (the cooling system must not be exposed to subzero temperatures) or very hot weather (the electronic equipment cannot be maintained at acceptable operating temperatures).

Importance of safety guidelines

Laser cleaning requires absolute adherence to certain safety guidelines. Each laser is categorised into one of four safety classes depending on the value of its accessible emission limit (AEL) in watts, which corresponds to its maximum emission. The machines used for cleaning stone are Class IV lasers, the most hazardous, with AELs greater than 500 mW. To give an idea of the danger of exposure to this type of laser, the glare of the sun is equivalent to an emission of 10 W per square centimetre. Cleaning lasers have a maximum emission level of 1010 W per square centimetre and are therefore a billion times more powerful than the sun! This level of laser energy can cause irreversible damage to the retina in the absence of protective eyewear!

Safety guidelines have been established for cleaning sites. The restorer handling the laser as well as all other persons working on the site wear special certified goggles that shield against the wavelength of 1064 nm (Photo 2). No reflective materials may be present in the working area. The laser is used in a closed space that may not be accessed by the public (Photo 4). The scaffolding must be fitted with a special frame, which is enclosed with a black tarpaulin or covered with wood panelling. All openings – windows, doors, etc. – must also be weatherstripped. An interior sensor indicates the arrival of an individual not part of the team at work on the site and will automatically turn off the machines. Laser operation is indicated by flashing red lights.

Photo 4: Interior of work zone on a laser cleaning site (restoration of the north portal of the Saint-Michel Basilica in Bordeaux (Photo: T. Vieweger).

In addition, as with any cleaning operation, the restorer wears a dust mask to avoid swallowing or inhaling fine particles that pose a potential health hazard. Along the same lines, but also to avoid the redepositing of removed grime nearby, a powerful vacuum cleaner is often directed at the region being cleaned.

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