LASER CLEANING OF STONE

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The beginning

Since the early 1970ies, laser technology was successfully applied for cleaning of artefacts. The first cleaning treatment with a laser was done on stone works in Venice by an interdisciplinary team leaded by J. Asmus in 1972 (1). A ruby holographic laser was modified and used for cleaning of the lion portal at Palazzo Ducale in Venice and other pieces of art made in marble. Although the cleaning results were convincing, for a longer time laser was only used seldomly. In some single cases C. Calcagno used the laser technology for cleaning some sculptures or ornaments made in bright marble or limestone.

Up to the middle of the 1980ies the interest for this technique increased in Europe. In France, Italy, Greece, Germany and Great Britain interesting cleaning projects with laser tools started to be carried out. Basic research was done improve the laser tools and to test it on a wide range of applications. Because of these efforts the laser tools became easier to handle and today they are suitable for work on scaffolding. From this moment the possibilities for cleaning have not focused only on stone materials. Laser cleaning technologies were also tested on metals, wood, ceramics, ivory, paintings, textiles and many other inorganic and organic materials.



Fig.1. One of the first laser cleaning projects at the beginning of the 1980ies was carried out by J.Asmus and G. Calcagno at the portal of the cathedral of Cremona in Italy

A hard way to convince

The responsible institutions in the field of care and protection of monuments and artworks are very careful and critical with new conservation techniques and so a lot of preliminary examinations and tests were carried out by scientists and conservator-restorers. In the field of stone conservation the laser cleaning technique is usually compared with other traditional techniques (e.g. micro sandblasting, paper pulp pad impregnated with an aqueous solution of ammonium carbonate and ion exchange resins (2). In many cases laser cleaning showed advantages and therefore some very interesting conservation projects could be done with Nd: YAG- lasers (e.g. Romanesque portal of Cremona (fig. 1), the portals of the Cathedral of Amiens (3) and Notre Dame in Paris, etc.). Especially on very delicate surfaces with thin scaling or brittle parts the laser offers the better alternative cleaning method, however problems have been observed in connection with some pigments and some binding media. In some cases the yellowing of some stone surfaces after laser treatment represents an esthetical problem.

Subsequently, a scientific platform was founded in Heraklion, Crete which was called LACONA (Lasers in the Conservation of Artworks), but there are also other national and international associations which are working



Fig. 2. Example: The inside of the Palladio Laser from Quanta Systems. The small box in the middle includes the artificial YAG crystal, which produces the monochromatic laser light (1064 and 532 nm). The transmission of the laser beam is caused by mirrors. This tool is qualified to the work on the scaffolding.

in the field of laser technology for artworks (e.g. COST G7).

Laser tool and function

At the moment there is a concentration of producing Nd: YAG lasers for stone conservation, although other laser types could also be successful for special cases. Presently, approximately five companies have YAG-Lasers in their production.

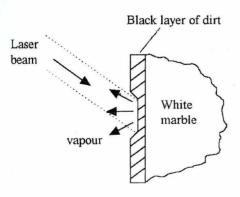
Common parameters of Nd:YAG-lasers are: wavelength (ë): 1064 and 532 nm, energy pulse energy (E): 250 – 1000 mJ and more, pulse width (t1): 6ns and more, repetition frequency (fp): 5 – 20 Hz and more, peak power (Ppk), average power (P) (W), beam diameter (non focused): 2 – 20 mm, different lenses, beam delivery: mirrors or cables made from glass fibre, focusing devices

(e.g. zoom optics). Recently the colleagues in Greece developed a modified laser system which combines ultraviolet and infrared laser radiation (4).

The process of cleaning with laser is done by evaporation (photo thermal ablation mechanism) and ablation/spallation (photo mechanical and photo chemical ablation mechanism) effects.

The intensity of absorption or reflection of the laser light, which is manly caused by the shooted substrates (stone, dirt, layers of over paintings, etc) is responsible for the quality of cleaning.

In the simplest case a bright white stone is covered by a black dark crust. After the evaporation of all black crust there is no dark material for absorbing the laser light and the light will be reflected without producing any damage for the white stone. This is also a reason why wet dirt is



Absorption of laser beam

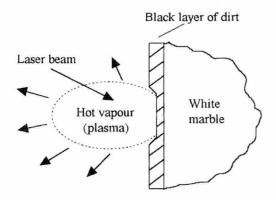
Reflected beam

Reflection of laser beam

Initial interaction of long pulse radiation with a dark encrustation. Strong absorption of energy leads to vaporisation of material.

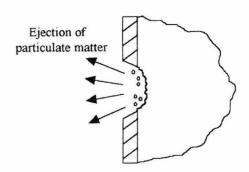
Figure 1.3. Normal-mode cleaning (Asmus, 1973).

Final interaction of long pulse radiation with a dark encrustation. Once the encrustation has been removed further pulses are reflected from the weakly absorbing marble surface.



Beginning of laser pulse

Vaporisation of encrustation occurs early during the pulse, leading to formation of a plasma. The temperature and pressure of the plasma increase rapidly as the incoming laser radiation is absorbed and a microscopic compression is applied to the surface.



End of same laser pulse

As soon as the laser pulse finishes the plasma expands away from the surface. The surface relaxes and a thin layer of material is ejected.

Figure 1.4. Removal of material by Q-switched laser radiation (Asmus, 1973).

Fig. 3. - figure 1.3. and 1.4, the laser cleaning process by John Asmus in Martin Cooper, Laser Cleaning in Conservation (5)



Fig. 4. half cleaned marble sculpture

easier to remove because it is darker. In reality such clear simple cases are rare and difficult situations are making the process of laser cleaning quite complex.

Base for laser cleaning

In the field of conservation (= cleaning) the most important parameters defining the conditions are the stone type and the nature of its surfaces as well as the presence of historical paint layers. The characteristics of the patina layers including black crusts, dust, soot and salts to be



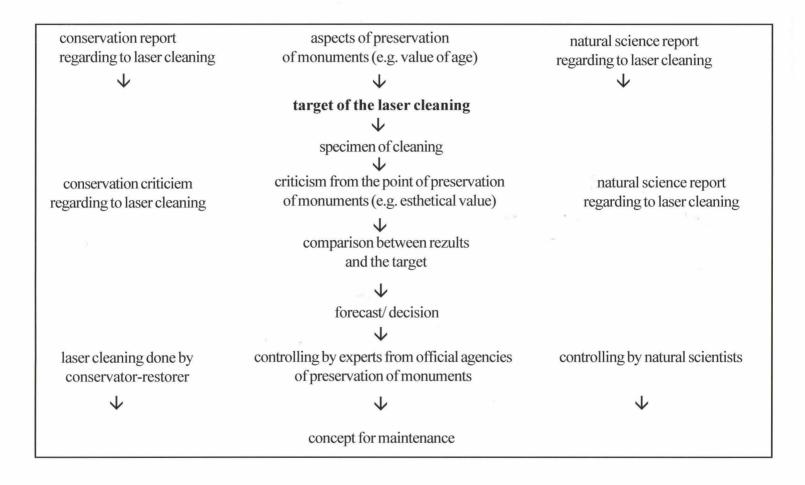
Fig. 5. Sensitive cleaning of scales on a sandstone surface

removed with the laser device are also important concerning the effect and speed of the cleaning process.

In principle every cleaning has to respect the signs of history and time because they are documenting the periods between creation and today. The task of laser cleaning is also connected with the "value of age" and other aesthetic values (**Table 1**).

Table 1: Principles of conservation and restoration in combination with laser cleaning:

Sandstone, calcareous sandstone, marble, red limestone



as well as other bright stone types have shown very successfully excellent results after laser treatments. The risk of undesirable cleaning effects has been reduced through foregoing appropriate cleaning samples and permanent scientific controlling. For special cleaning problems e.g. white marble surfaces with sandy scaling the laser tool can preserve even delicate surface details, which are often identified as last preserved original stone surfaces (**Fig.4 and 5**). A big advantage can also be the possibility to clean without pre-consolidation (e.g. ethyl silicate, acrylic resins, silicon resins and other mixtures). In this case laser cleaning can often be faster than other

cleaning techniques.

Stone material where Laser was applied successfully:

- bright marble: Carrara marble, Laaser marble, Penthelicon marble, Carinthian marble,...
- sandstone: Types of quartz sandstone (e.g. Wienerwald-Flyschsandstein), types of calcareous limestone (e.g. Margarethner or Zogelsdorfer stone)
- compact limestone: Istrien stone, Untersberger limestone, Verona red, Adneter red.





Fig. 6. Photo from a cross section of a red limestone under the light microscope before and after laser cleaning

Concrete, artificial stone and different types of mortars

• casein layers from former conservation treatments

Material that could be removed from stone surfaces:

- black crusts
- thin concrete layers
- dust and soot
- old acrylic and epoxy layers from old treatments

From the economical point of view the comparison between traditional and high tech cleaning systems is very important. Often the best cleaning result can be achieved by combining three or more cleaning techniques, including also laser treatment for special purposes (**Table 2**).

However, if there are monochrome or polychrome layers,

Table 2 Example: Comparison of different methods of cleaning at the Romanesque west portal of St. Stephens Cathedral in Vienna:

tool or material	location	result	time in minutes/dm ²
abrasive gums, wish-up and fine brushes	ornamented vault ornaments inside	pre-cleaning	30
vacuum cleaner	all surfaces	before pre-cleaning	1
compresses (9 x) and fine brushes	columns, ornamented vault, flat surface inside	pre-cleaning (only by salty areas)	45
precise whirl blasting (low pressure with dolomite powder)	flat surface outside	pre-cleaning	10
micro sand blasting with different powders	flat surface inside cornices	pre cleaning	15
	flat surface outside	final cleaning	20
laser cleaning with high energy	sculptures and ornaments outside, flat surface inside	final cleaning	20
laser cleaning with low energy	ornamented vault columns, sculptures tympana (all details	final cleaning	15
compresses with ammonium carbonate	figurative consoles outside	additional cleaning	20



Fig. 7. How do protect yourself during laser cleaning

cleaning with Nd-YAG lasers is possible only in rare cases.

It is also very important for the conservator-restorer to follow safety regulations thoroughly. Protection with special glasses for the eye, gas-mask, appropriate cloths, exhauster and a right isolation with a sign for danger of the working place (studio, scaffolding, work shop) where the laser is used is an absolute mandatory.

Applied to stone conservation the laser technique is not only used for cleaning but also for laser diagnostics (e.g. holography, vibrometry), 3D-measurements for monuments and artworks (documentation tool) and spectroscopy for monitoring and identification (e.g. RAMAN, LIBS, LIF).

Prospects

There is a great attention to side effects caused by laser cleaning (short- and long-term), including the behaviour of pigments and binding media, removal of former conservation layers, fundamentals of laser-artwork interaction (yellowing), recent laser developments for cleaning (e.g. uncommon wavelengths, short/long pulse), laser cleaning stations for practise (in situ/atelier/lab), standardization, safety and health aspects and many other connected contents.

In Austria the use of laser cleaning in the field of conservation was introduced in 1995. During the last 10 years a lot of different stone monuments and historical



Fig. 8. St. Stephens cathedral, west portal after laser cleaning and conservation

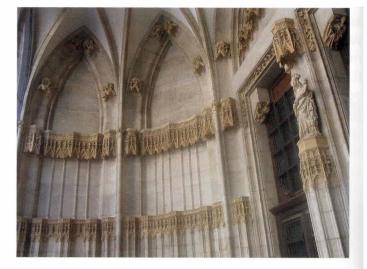


Fig. 9. St. Stephens Cathedral gothic portal under the south dower after laser cleaning

facades were cleaned by laser technique (e.g. Romanesque and Gothic parts from St. Stephens Cathedral (Fig. 8 and 9), marble sculptures from the parliament and public gardens, Gothic outdoor sculptures and facades from many other churches and buildings). Four different types of modified Nd:YAG-lasers were used.

The cooperation with Romania started 6 years ago during the Action COST G7 (Lasers for artworks conservation), an European project, which was initiated by a Romanian colleague (Roxana Radvan). Meanwhile the laser is used in Rumania also for very delicate pieces of artworks and monuments.

An example:

The tomb of an Austrian Minnesingers called Neidhart Fuchs is one of 140 other grave monuments outside of St. Stephens cathedral. It was made around 1360 and consists of a rectangular stone tomb, a formal reduced lying sculpture and a relief torso. The sculpture and the relief torso are made out of local calcareous sandstone. Originally these parts of the tomb had a totally polychrome surface. The coloration was very intense and the oil-painting was painted directly on the stone, without first ground. The used pigments are: cooper green for the hat, minium and lead white for the colour of the skin, azurite for the habit and the bolster with an inner-painting in lead-tin-yellow, iron-oxide-red for the hair, cinnabar for the outer-coat, ochre as ground for the gilding of the belt and lead-tin – yellow for the background of the coat of arms. But only traces of these colours can be found on the original surface. Most surface areas of the sculpture are reduced by weathering, black-crustformations and mechanical damage. The stone shows a lot of cracks, a loss of binder under the black crust and a high amount of chlorides and nitrates. The cleaning, conservation and restoration is based on the results, which was applied at the west portal of St. Stephens Cathedral.

According to the different conditions of the deposits partly first individual pre cleaning has been made with common methods as abrasive gums, compresses with paper pulp and ammonium carbonate, pneumatic micro tools and micro sandblasting.

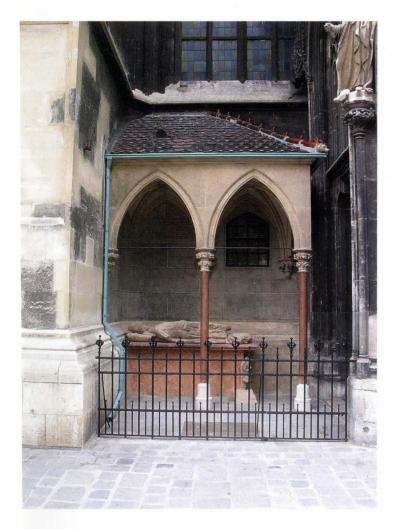
But most surface areas were cleaned by laser tool. In some cases sensitive pigments did not allow the laser treatment (e.g. cinnabar) fig.

In the contrary to the other cleaning methods laser was the most sensible. In any case we found important to know where and which colour was left under the black crust because of the specifically reaction from the laser with pigments and the painting media. The laser, which was used was the pulsed Palladio Nd.:YAG laser from ALTECH (parameters of the tool: 1064nm, 6nS, 5-15Hz, 350-650mJ, size of the laser spot 6-10mm, different lenses).

The facade of the cathedral behind the grave was painted under the black crust with ochre and grey lime washes



Fig. 10. The tomb before laser treatment



Fig, 12. The tomb after laser cleaning and conservation



Fig. 11. the sculpture of the Minnesingers during cleaning

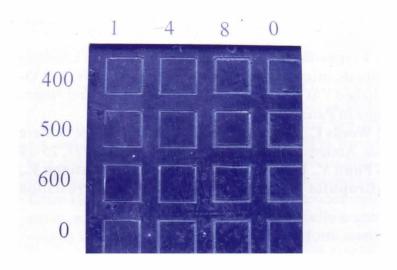


Fig. 13. Ultramarine and azurite shows no changing of the pigments after the laser treatment. 1, 4, 8, 0, are the numbers of laser shots. 400 (ca. 260mJ), 500 (ca. 330mJ), 600 (ca. 400mJ) are the different levels of energy

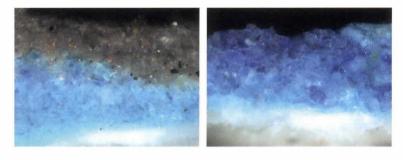


Fig. 14. Photo from a cross section of an azurite layer under the light microscope before and after laser cleaning

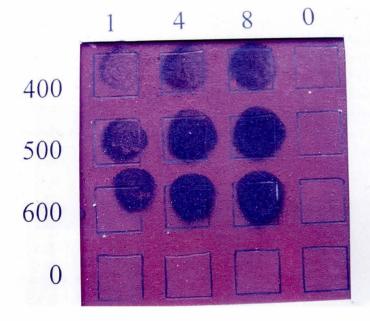


Fig. 15. Cinnabar and lead tin yellow shows total blackening on test areas after the laser treatment

and dark joints. This surface also was cleaned by laser and ammonium carbonate compresses.

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