Laser cleaning of Rakowicze sandstone

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Decisions about the cleaning of natural stone should always be made within the awareness of direct and indirect damage that may be the result of cleaning. During the last decade, laser cleaning of objects and monuments of natural stone has become increasingly popular. Whereas a considerable amount of literature has been devoted to the effect of laser cleaning on marble and limestone, research into the effects on sandstone is limited. In the present paper, the effect of two cleaning methods, viz. the combination of dry microblasting and laser and laser alone, on Rakowicze sandstone that had developed a thin black weathering layer, are reported and evaluated. Results of visual inspection, microscopic investigation and determination of water absorption and evaporation behaviour are enigmatic.

Key words: Natural stone, Rakowicze sandstone, laser cleaning, black weathering, damage, microscopy

1 Introduction

Cleaning of monuments made up in natural stone has been proliferating all over Europe. In The Netherlands too, more and more monumental buildings have been cleaned over the last decade. The cleaning of historic monuments is (generally) disapproved off by the Dutch conservation autorities because of the risk of damage to the natural stone and monument as a whole (e.g. RDMZ 1999). This damage may be divided into direct damage and indirect damage (Wijffels 2000). An example of direct damage is the loss of the surface of a brick due to cleaning with sand blasting technique. Also fine sculpture or working in natural stone may be lost in this way. Indirect damage is damage which occures after the building was cleaned, due to changes in the properties of the material. Due to the cleaning, the façade may be more vulnerable to frost and salt damage. Because of these risks, conservation autorities in the Netherlands do not give permission to clean a historic monument, unless research proved that cleaning will not damage the façade.

Over the last years, a novel cleaning technique, viz. the use of laser, has been coming more and more in vogue to clean statues and other works of art (e.g. Kautek & König 1997, Cooper, 1998). As far as natural stone is concerned, most research into the effects of laser cleaning have been devoted to objects out of marble or limestones. Recently, cleaning by use of Nd:YAG lasers is applied to entire buildings (e.g. Pini et al. 2000). The fundamental wavelength of a Nd:YAG laser (λ = 1064 nm) is nowadays the most established laser wavelength for cleaning stone surfaces.

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Though the use of laser techniques to clean façades may be promising, hardly any research into both the risks of direct and indirect damage to natural stone façades in general, and objects in sandstone in particular, is available. Limited studies on sandstone related to the determination of ablation threshold fluence of the laser in J cm-2 (Klein et al. 2000), i.e. the values below which no material is removed from the black weathering layer and sandstone itself, respectively. Laser cleaning is feasible if the employed fluence of the laser is within the threshold gap, i.e. higher than the ablation threshold fluence of the black weathering layer, but lower than that of the sandstone. Threshold values are assessed by determining (gravimetrically) the amount of material removed at a certain fluence. There is no experience in long-term effects of laser cleaning, for example possible chemical / mineralogical modifications of the stone and its microstructure, or loss of quartz grains due to other mechanisms than ablation (Klein et al. 2000). In case of stained glass, laser pulses below the ablation threshold fluence have sufficient energy to change its physio-chemical properties (Troll et al. 1999). Colour changes induced by laser treatment have been documented from many materials. Nd:YAG laser operating at its fundamental wavelength has been shown to cause blackening of pigments (Eichert et al. 2000), yellowing of marble (e.g. Klein et al. 2001, Marakis et al. 2003), blackening of veined Carrara marble (Eichert et al. 2000) and greyish alteration of fresh Carrara marble (Aldrovandi et al. 2000). In case of the Carrara marble, colour changes were attributed to oxidation of Fe^{2+}, and microexplosion around pyrite grains at short laser pulses (20 ns), and fusion combined with spread of particles on the surface at medium laser pulses (20 μs), respectively.

Klein et al. (2000), working on Elbsandstone, observed a slight change of colour of the sandstone after cleaning. Jankowska & Śliwiński (2003), studing Nd:YAG laser cleaned sandstone in which quartz grains were cemented by loam and calciumcarbonate, found that after cleaning, the cement in the surface layer below the removed black weathering layer was lacking, but that no quartz grains had been removed or damaged; from their observations, it is unclear whether the carbonate cement was removed by laser, or had previously reacted to gypsum. Siano et al. (2000), studying the effect of Nd:YAG laser on Pliocene sandstone from Siena observed the darkening of fresh quarry samples, which they attributed to the selective removal of the carbonate component from calcareous cement containing Fe-(hydr)oxides (limonite). In the current paper, the results of an investigation to the effects of laser cleaning of Rakowicze sandstone are reported.

1.1 Rakowicze sandstone

The Rakowicze sandstone is a greyish yellow sandstone from the Lwówek Śląski district in Silezia, Poland. It has been designated as Rackwitzer Sandstein in Germany and Silezian or Rachwitz sandstone in the Netherlands. It is a quartz-rich, open sandstone (Fig. 1) with part of the pores filled by clay minerals (Fig. 2), which also occur as thin coatings on detrital quartz grains. Locally in the samples, domains with a considerable amount of Fe-(hydr)oxides occur, pointing to an originally sideritic or ankeritic cement.

The Rakowicze sandstone has been quarried since the 16th century, and applied to many monuments in Poland, Germany and The Netherlands. In the Netherlands, Rakowicze sandstone has been applied during the 1910's – 1930's, amongst others to the former building of the Koninklijke

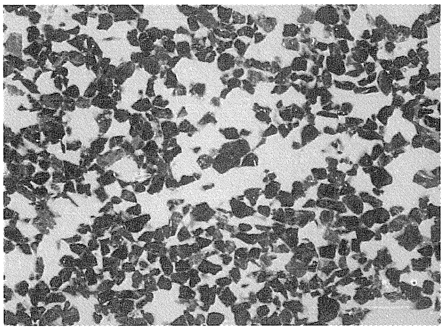

Fig. 1. UV-fluorescence microphotograph showing the open structure of fresh Rakowicze sandstone (view 5.4 x 3.5 mm).

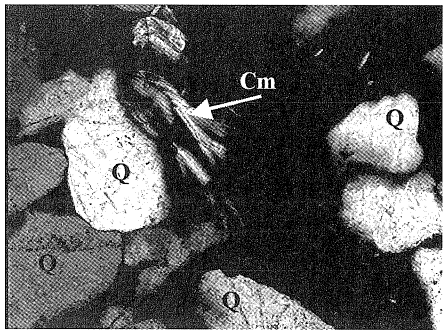

Fig. 2. Microphotograph showing pore filling of clay minerals (Cm) between quartz (Q) grains (cross polarized light, view 0.7 x 0.45 mm).

Hollandsche Lloyd at the Oosthandelskade, Amsterdam, and the town halls of Rotterdam, Noordwijk and Waalwijk. In Germany, the Rakowicze sandstone has, amongst others been applied to Berlin's Brandeburger Tor.

In case of the present façade, the black weathering layer on Rakowicze sandstone was very thin, generally less than 1/3 of the size of the quartz grains (Fig. 3). The black weathering layer forms a very thin film on the quartz grains, whereas pores open to the surface may also have been filled (Fig. 4). Components identified in the black weathering layer include soot, fly ash and Fe-(hydr)oxides, which are probably fixated by gypsum. Remains of algae, common in black weathering layers on Bentheim and Obernkirchen sandstone in the Netherlands (Nijland et al. 2004ab), have not been encountered.

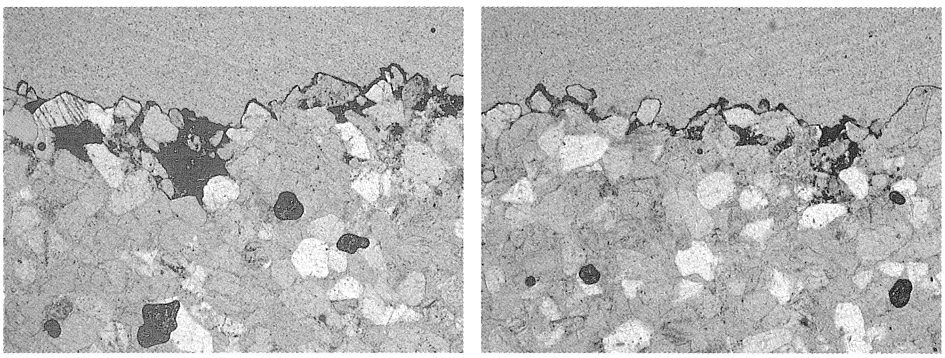

Fig. 3. Overview of black weathering layer on Rakowicze sandstone (view 5.4 x 3.5 mm).

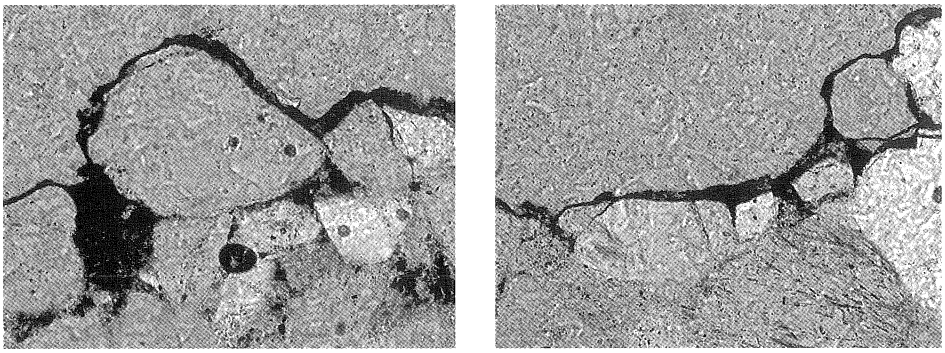

Fig. 4. Detail of black weathering layer on Rakowicze sandstone (view 0.7 x 0.45 mm).

2 Cleaning

The Rakowicze sandstone was cleaned using two techniques. In one case, the material was treated by dry microblasting after which the sandstone was cleaned using laser, in the other, only laser was applied. The aim of the research was to determine whether:

- the combination of the two techniques led to the best results;
- cleaning led to any direct damage;
- cleaning may lead to any indirect damage.

The research was carried out using four test panels. These panels were part of one large monolithic block of sandstone, selected after inspection of the façade. The sample was selected for its representativity for the façade. The sample had one single homogeneous black weathering layer, without significant variation in intensity of the black appearance.

The first panel was not cleaned and preserved its black weathering layer. The second test panel was only treated by dry microblasting, and the third with a combination of both dry microblasting and laser cleaning. The last test panel was cleaned with laser but without treatment by microblasting. Dry microblasting was carried out using aluminosilicate. Figure 5 shows this material enlarged by the microscope. The glass-like particles are clearly sharp edged. Laser cleaning was performed with a commercial class 4 Q-switched Nd:YAG laser operating at 1064 nm.

After cleaning, test panels were evaluated and compared. The evaluation of the present of direct damage to the surface was carried out by visual inspection and polarization-and-fluorescence microscopy (PFM). The evaluation on the risk of indirect damage took place based on the water absorption of the cleaned material and the drying speed.

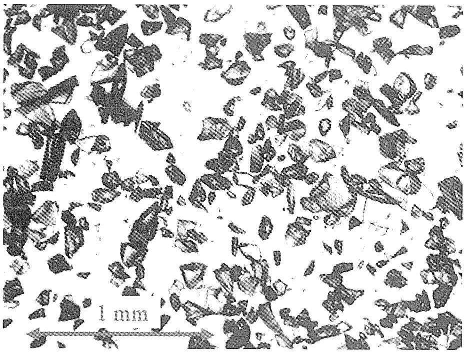

Fig. 5. Aluminosilicate used for dry microblasting.

3 Results

3.1 Visual inspection

Laser cleaning changed the colour of the test panels from black to greyish yellow. It should be realized that fresh Rakowicze sandstone has a greyish yellow colour of its own, and no connotation with so-called 'laser yellowing' (cf. Klein et al. 2001, Vergès-Belmin & Dignard 2003) is implied. The result is evidently a shift in colour and appearance towards that of fresh Rakowicze, though some shades of weathering are still visible. In case of the combination of with dry microblasting, the appearance of the Rakowicze sandstone was less bright than the material cleaned with laser only. This difference is visible on Figure 6. The left shows the test panel cleaned by combination of dry microblasting and laser, the right the panel cleaned by laser only. This result seems remarkable because with less effort an apparently more clean surface was obtained.

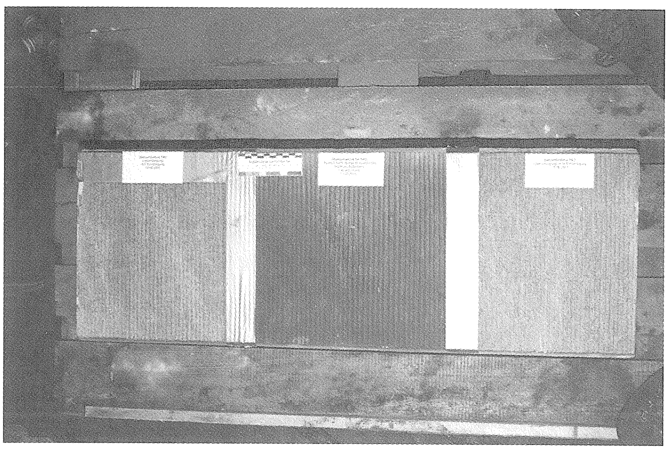

Fig. 6. Test panel of Rakowicze sandstone. In the middle, non-cleaned stone, as removed from the façade, flanked to the left by a part cleaned by the combination of dry microblasting and laser, and to the right a part cleaned by laser only.

3.2 Polarization-and-fluorescence microscopy (PFM)

Whereas visually, a difference is present between the result of cleaning by combination of dry microblasting and laser compared to cleaning by laser alone, microscopically no clear difference is present. In both cases, the thin black film on the quartz grains has been removed (Figs. 7, 8). Within the black weathering layer, the amount of material filling pores open to the surface is quite variable. Nevertheless, it appears that, in case of cleaning by laser only (Fig. 8), more of this material remains after cleaning than in case of cleaning by combination of dry microblasting and laser (Fig. 7). This is effect is, however, variable over the surface. In both cases, none of the original quartz grains are removed, and the sandstone itself is not directly damaged.

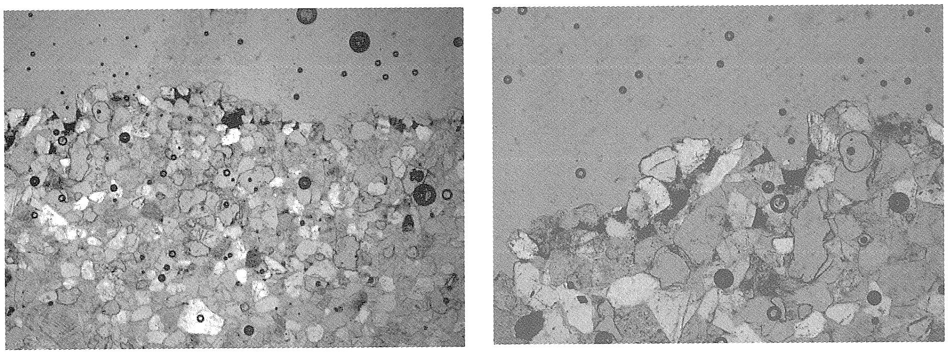

Fig. 7. Microphotographs showing an overview of surface of Rakowicze sandstone after cleaning by combination of dry microblasting and laser (view 5.4 x 3.5 mm left, 2.7 x 1.4 mm right). Note that the black material on top of the quartz grains has been removed, but that it is still present between and below the grains.

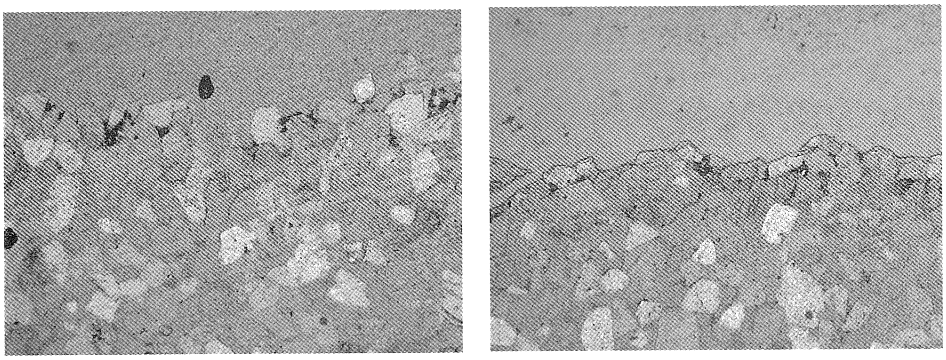

Fig. 8. Microphotographs showing an overview of surface of Rakowicze sandstone after cleaning by laser only (view 2.7 x 1.8 mm).

3.3 Water absorption

The water absorption was measured on specimens of 5 x 5 cm cut out the test panels. These specimens were sealed on the lateral sides. The surface was brought in contact with water and the water uptake was measured every minute. This experiment was carried out in fivefold.

Figure 9 shows the results of the water absorption. On the horizontal axis the time is given in the square root of time in seconds. The graph shows that the speed of water absorption of the non-cleaned material is less than that of the cleaned sandstone. Water absorption is the highest in the materials which was cleaned by laser only. Especially at te start, there is a difference in water absorption between the three test panels. The water absorption of the laser-cleaned sandstone is clearly not limited by the surface. From the start, absorption in square root of time is linear. This is not the case for both the non-cleaned sandstone and the sandstone cleaned by combination of dry microblasting and laser.

The results of the water absorption agree with the visual impression of cleaning. By using laser only, the surface of the Rakowicze sandstone is changed to a larger extent than in case of laser cleaning in combination with dry microblasting.

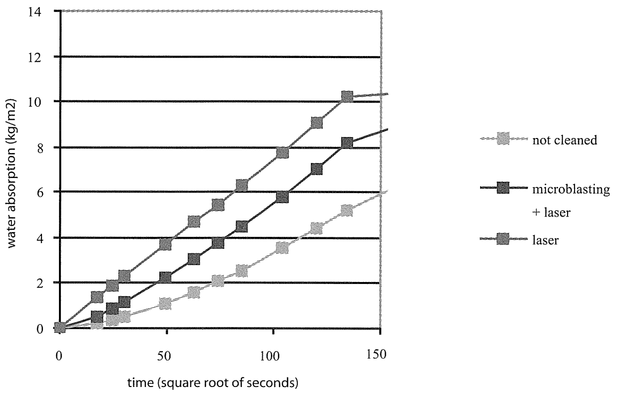

Figure 9. Water absorption

3.4 Drying rate

The drying rate was measured on the same specimens that had been used for determining water absorption. After saturation by capillary absorption, the specimens were stored in a climatic cabinet at 20 °C and 50 % RH. The evaporation was measured daily (Fig. 10). The first days there is hardly any difference between the drying speed of the cleaned sandstone. The drying rate of the non-cleaned material is slightly lower. After about 10 days, drying of sandstone cleaned by combination of dry microblasting and laser only slightly differs from that of the non-cleaned stone, in contrast to that of sandstone cleaned by laser only (Fig. 10).

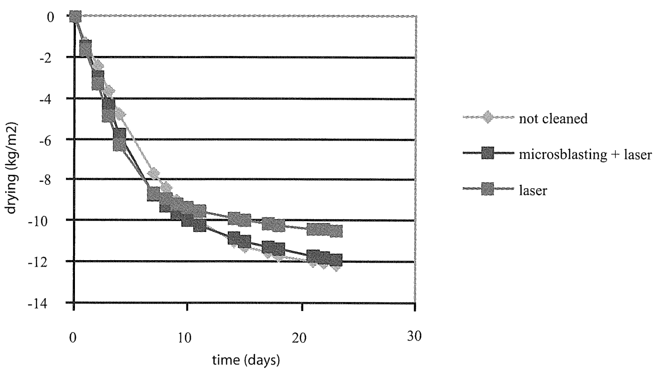

Figure 10. Drying

4 Discussion

Microscopic investigation showed that no direct damage occurred to the Rakowicze sandstone itself. Quartz grains were not removed, nor damaged, as also observed by Jankowska & Śliwiński (2003). The thin black film on top of the quartz grains was removed by both laser cleaning and laser cleaning in combination with dry microblasting. The material below and in between the quartz grains was (generally) not removed by any of the techniques. The visual appearance of the sandstone was changed towards its original greyish yellow colour, with shades of colour determined by the original colour of the stone and material remaining in the pores near the surface (and hence by variations in porosity arising from grain size variations, variations in amounts of diagenetic pore fillings etc.), and, by consequence, not becoming near the aesthetic appreciation of a freshly cut stone.

Indirect damage is generally due to a high water content. Damage mechnisms as frost and salt crystallization are related to water. To evaluate the risk of indirect damage due to a cleaning, the hygric behaviour of the stone should be compared to both the uncleaned stone and the fresh material. Water content of a natural stone in a façade is dependent on both the water uptake and the loss of water as a result of evaporation. Water absorption is significantly increased by the cleaning (Fig. 9).

There seems to be a difference in water absorption between the two cleaned test panels. In the panel which was cleaned by laser only, the rate of water absorption was linear. In case of both the non-cleaned material and the sandstone cleaned by combination of dry microblasting and laser, the rate of absorption increased after a slow start. In case of the non-cleaned sample, this slow start is likely due to the fact that the surface is open over only a limited area. It is enigmatic why the sample cleaned by combination of dry microblasting and laser shows comparable behaviour, and the material cleaned by laser only has an apparently more absorbing surface (Fig. 9). As only three panels have been investigated, it could not be evaluated to what extent variable amounts of diagenetic pore fillings, notably clay minerals, in the sandstone contributed to this. With respect to evaporation, no significant difference was found between both cleaned panels.

5 Conclusion

Microscopic investigation clearly shows that the Rakowicze sandstone did not suffer any direct short-term damage from either cleaning method. Effects on visual appearance and aesthetic appreciation as well as hygric characteristics are, however, enigmatic and should be subject to further research. Visually, the result of cleaning by laser only is superior to that of cleaning by dry microblasting followed by laser, if judged in terms of greyness. In addition, water absorption of the sample cleaned by dry microblasting in combination by laser appeared to be more similar to the original stone as removed from the façade, i.e. with its black weathering layer, whereas the sample cleaned by laser only showed strongly increased water absorption. Evidently, more research into the effect of laser cleaning on sandstones in general is needed.

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