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Acoustic monitoring for the laser cleaning of sandstone

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Abstract

For the laser ablation of crust on historical sandstone samples contaminated due to prolonged interaction with the environment, and also for specimens covered by artificial crust layers, the potential of acoustic monitoring is examined. Measurements of the snapping sound amplitude vs. the deposited laser energy carried out for dry, moistened and wet samples at laser fluences in the range of 0.1–3 J cm^{-2} (Nd:YAG, 6 ns, 1064 and 532 nm) confirm the advantages of wet cleaning. The exponential decay of the signal corresponds to a similar decrease of the crust thickness, characterized by an average rate of about 10–14 μm per pulse, and the data of original samples reveal better reproducibility compared to those of the model crust. From data analysis, a narrow band of the reference signal of 8.5–11% of the maximal one follows, which corresponds to the crust-free surface, and for parabolic dependences of both sound amplitude and cleaning speed vs. laser fluence, the clear maxima agree with optimal processing parameters. The strong correlation observed between the acoustic signal and the ablation progress supports the conclusion of the usefulness of acoustic monitoring for laser cleaning of stone artefacts.

Keywords: Sandstone monuments; Laser cleaning; Acoustic monitoring

1. Introduction

For the diagnosis and monitoring of the laser restoration of stone artefacts, the characterization of the substrate and encrustation material before, during and after removal of the surface pollutants is essential. There are analytic techniques that have been successfully applied, such as the spectroscopic ones, i.e. laser induced breakdown spectroscopy, laser induced fluorescence and Fourier transform infrared spectroscopy, which deliver information on the chemical composition and morphology of the materials. The surface inspection methods of energy dispersive spectroscopy, scanning electron microscopy, X-ray diffraction and optical microscopy are also used to assess the effects of laser interaction and to characterize the topology of the surfaces. These techniques are reported for laboratory experiments as well as works on site [1–3].

Ablation studies represent an important contribution to this research. For the case of laser removal of black encrustation on stone by means of a pulsed Nd:YAG laser operating at 1064 nm, ablation rate values around 10 μm per pulse at fluences of about 3 J cm^{-2} are reported, which corresponds to about 0.1 nm per incident photon [1]. Recently, the potential of the UV radiation range for the cleaning of stone monuments has been examined, and results regarding the application of KrF excimer laser (248 nm) have been reported [4]. It follows from the case studies that the maximal efficiency of photon energy conversion into cleaning of 37% for a Gaussian beam intensity distribution can be increased up to 90% by the application of a flat intensity profile (top hat), while the laser fluence should be kept as close to the ablation threshold value as possible in order to prevent damage and bleaching of the stone material [5]. Detailed investigations of the photoablation dynamics on the time scale from milliseconds to nanoseconds allow an understanding of the relevant physical effects [6–8].

In the case of laser cleaning of historical stone objects that have been sufficiently characterized, after selection of the laser, it is important for the conservator to control the possibly low number of parameters required for process monitoring. The detection of the acoustic signal due to the shock wave accompanying material removal represents an interesting and cost-effective solution to the above problem [9].

In this work, experimental studies on the acoustically monitored laser cleaning of historical sandstone samples

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covered by a black, porous encrustation, as well as of model specimens with artificial coverage, are reported. The ablation studies are carried out with a pulsed Nd:YAG laser operating at 1064 and 532 nm for moistened, thoroughly wet and dry samples. The threshold values for laser ablation of the investigated materials are measured. It is shown that the acoustic signal correlates strongly with the progress of the crust ablation process, thus allowing for reliable monitoring. Dependences of sound amplitude on the laser interaction parameters, the crust thickness and the degree of moistening are discussed. The optimal parameters of the ablation process and those of the recorded sound intensity are derived and discussed.

2. Experimental

Samples of a light yellow sandstone from the collection of sculptures and facade elements preserved at St. John's Church in Gdansk have been selected for irradiation experiments. The samples originate from Swedish quarries, which delivered material during the cultural and commercial boom the city experienced during the XVI–XVII century. The sample surface was originally covered by a porous, black crust due to interaction with an atmosphere polluted by industry and combustion and also with marine spray typical in areas close to the Baltic Coast.

Also, a set of artificial crust samples for the simulation and modelling of the laser cleaning of sandstone was produced according to a standardized procedure, described elsewhere [7]. Each sample was composed of a 5-cm-thick substrate of yellow sandstone covered by two deposited layers. The first one was a 100-μm-thick coating of calcium oxalate, representing the natural patina, which should be safeguarded by the restoration. The second layer of black gypsum was deposited onto the first layer in order to simulate the degraded substance to be removed by laser ablation. The black gypsum applied was a mixture of gypsum, carbon black and quartz in a ratio of 100:12:1. A linear variation of the crust thickness in the range of 0.1–1 mm was employed, and the layer was carefully dried after preparation.

For sample irradiation, the pulsed Nd:YAG laser (Quantel) operating in a Q-switched, single pulse mode characterized by a pulse duration of 6 ns was used. The wavelength selection has been assured by addition of the second harmonic generation module (SHG). The laser beam was directed onto the sample surface by an optical train consisting of bending mirrors (BK-7). A telescope composed of two spherical lenses (BK-7; $f = 250$ mm) assured the control of the beam position and focusing. During the experiment, a constant pulse energy of 290 mJ per pulse was applied and measured by an energy meter (Gentec). This assured an exact selection of the laser fluence in the range from 0.1 to 3 J cm^{-2}, by changing the distance between sample and telescope. For the ablation measurements, the samples were irradiated perpendicular to the surface, and the laser was operated in the single pulse mode. A selected area of the surface was laser treated till the crust was completely removed.

An electret microphone was applied for detection of the snapping sound accompanying the laser pulse interaction. Depending on the sample under investigation, the detector was placed behind of the stone sample close to its back surface or to the front of it. The angle of signal incidence onto the detector was kept constant and close to the normal to the stone surface. After extraction of the background acoustic noise, the signal was recorded with a digital oscilloscope, TDS 3012 (Tektronix), and the signal traces were stored and processed using a PC based data acquisition unit. It was assumed that the recorded sound intensity was independent of the frequency. The measurements of the sound amplitude dependence on layer thickness were repeated for several areas of the sample in order to assure better statistics of the measured values.

3. Results and discussion

3.1. Encrustation removal and ablation threshold

For sample irradiation, the fundamental wavelength of 1064 nm, as well as the output of the SHG module of 532 nm, was applied in order to find the optimal performance conditions.

The ablation threshold, i.e. the highest value of laser energy per pulse and unit surface that does not result in material removal due to photoablation, was measured for previously untreated original sandstone elements covered with the black crust and for the artificial specimens as well. The measurements were carried out for dry and moistened surfaces, and the threshold values for irradiation at 1064 nm of 0.40 and 0.10 J cm^{-2} and, for the case of 532 nm, of 0.10 and 0.06 J cm^{-2} were obtained, respectively. These results characterizing the original crust are in good agreement with those reported for the removal of a dendrite-like black crust from limestone by pulsed Nd:YAG laser at 1064 nm [10]. It is to be observed that values measured for the 532-nm laser are markedly lower, which could indicate more efficient energy use due to higher absorption at this wavelength. On the other hand, the use of the 1064-nm radiation for stone cleaning is preferred, because the value of crust absorption of 60–80% is about two times higher than that of the stone material [9,11]. This absorption difference leads to interaction selectivity, which supports the conservation task in that it lowers the possibility of damage to the stone material underlying the encrustation to be ablated. The conclusion regarding preference of the 1064-nm laser for the restoration of stone artefacts has been confirmed experimentally for limestone, marble, alabaster and sandstone by other authors as well [6,9,12].

The ablation rate of the black encrustation layer on the sandstone was estimated from microscopic observations and from the profilometer study, where a typical crater of 1.8 mm diameter resulting from a single laser pulse was investigated. Values of about 10–14 μm per pulse (1064 nm, 1 mJ cm^{-2}) are in agreement with those following from an experiment for the removal of a 360-μm-thick encrustation after a given number of pulses. For the model encrustation, the ablation threshold was measured exclusively for the wet sample. Visual observations revealed that at the fluence level of about 2–3 J cm^{-2}, which has been assumed to be the operative range for the cleaning of sandstone, the calcium oxalate patina underlying the black gypsum deposit was not affected by the laser radiation, and for energy densities below 2 J cm^{-2}, ablation of the crust was not observed. A similar threshold value for ablation was measured for an original crust irradiated by KrF laser (248 nm) as well [4]. This confirmed that the chemical composition of the model layer was selected correctly, thus representing a response to the laser interaction comparable to that of the original crust.

3.2. *Monitoring of crust removal from original sandstone samples*

For the dry and wet surfaces, the sound intensity amplitude was monitored vs. the number of pulses at various levels of laser fluence above the ablation threshold for the irradiation wavelengths of 1064 and 532 nm. A reference acoustic signal corresponding to the encrustation-free surface was obtained for the arbitrarily selected fluence of 0.38 J cm^{-2}. An example of a stone object cleaned by the laser technique is shown in Fig. 1. The experimental data collected for the case of a wet and a dry surface are shown in Figs. 2 and 3. The error bars corresponding to fluctuations of the laser pulse energy, observed typically in the range up to ± 4%, are not shown, for simplicity. The signal maximum measured for the second laser pulse is characteristic for water assisted cleaning (see Fig. 2). The first pulse evaporates mainly the thin water film covering the crust, which results in a lower signal. Exponential dependence of the measured sound intensity on the energy dose is observed for the entire range from 0.16 to 0.55 J cm^{-2} of applied pulse energy. A dramatic decrease of the signal by a factor of 3–4 can be observed in all cases, and values close to the reference one are obtained already after the first five laser pulses. The next few pulses result in a slower signal fall, and the asymptote at about 0.14–0.2 V, corresponding to the non-contaminated sandstone surface, is obviously reached after 10 pulses. A constant value of the sound intensity close to the reference level observed for prolonged irradiation confirms that the cleaning process has been finished. It also assures that for the selected irradiation conditions, no detectable damage of the surface occurs. This is in agreement with the results of optical inspection and with the literature data regarding the self-limiting of the ablation effect [1].

Fig. 1. Surface of the test sample wet cleaned by means of laser ablation: Nd:YAG laser, 1064 nm, 6 ns pulse duration.

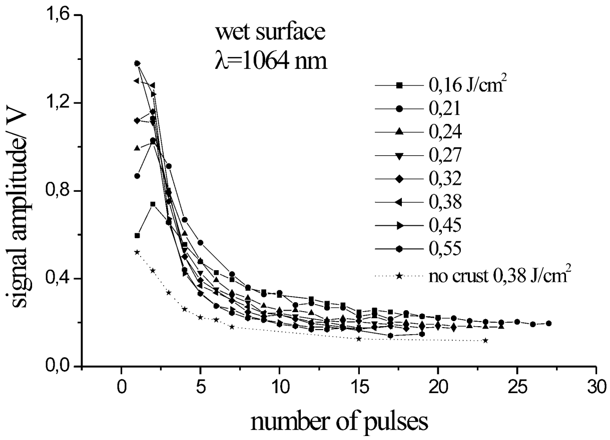

Fig. 2. Dependence of the acoustic signal amplitude on the laser pulse number; yellow sandstone; experimental conditions as in Fig. 1.

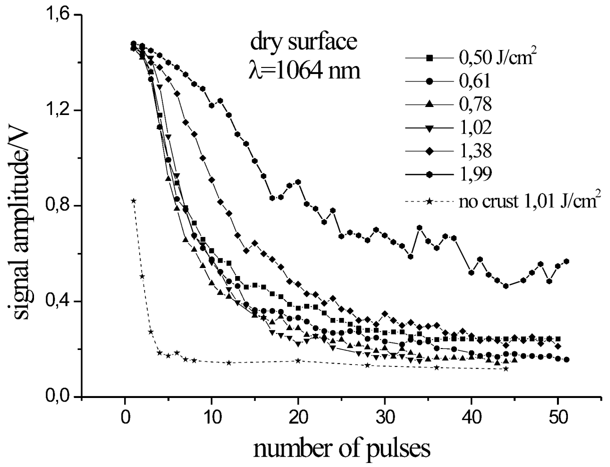

Fig. 3. Same as Fig. 2; data for the dry surface cleaning.

In the case of dry cleaning, a similar, exponential fall of the sound intensity was observed. The data obtained for 1064-nm irradiation are shown in Fig. 3. However, higher laser fluences in the range of 0.5–2.0 J cm^{-2} and also greater pulse numbers were necessary to achieve a processing result comparable to that of wet cleaning. The experimental data were characterized by stronger signal fluctuations. This was due to the fact that the acoustic waves accompanying the laser interaction were not damped by the presence of liquid. The maximal sound intensities of about 1.47 V did not depend on the laser fluence applied, and the reference signal of about 0.13–0.21 V (crust-free surface) corresponded to that detected for wet cleaning. An up-shift of the reference signal together with a decreasing slope of the exponential signal decay was observed at fluences above 1.4 J cm^{-2}, and the effect was even more impressive for the 532-nm laser applied. This was accompanied by a slight flashing of the laser interaction area at fluences above 3 J cm^{-2}. This indicated not only that the laser pulse led to explosive evaporation of the sandstone contaminant, but also that optical discharge (OD) over the surface was initiated. However, the post-processing damage of the sandstone surface has not been observed. The above observation leads to the conclusion that for laser fluences above a given level, and particularly for dry cleaning, the acoustic signal of interest also contains a component originating from OD. On the other hand, the observed effect does not seem to limit the usage of acoustic monitoring, as the optimal process parameters lie far below this fluence level, as will be discussed further in the text.

For the laser operating at 532 nm, the experimental data were collected and processed similarly. Results of acoustic monitoring of the wet and dry laser cleaning at 1064 and 532 nm are summarized in Fig. 4a, b. Interesting conclusions can be drawn from the example of data for the wet cleaning and laser fluences not far above the ablation threshold, together with those extracted from measurements with the 1064-nm laser for comparison (Fig. 4a). It follows that the 532-nm laser assures milder interaction conditions. Differences in slopes of the curves for 532 nm indicate that the process is even more efficient at lower fluence. However, the highest slope corresponding to the shortest time required for the crust to be removed is measured for the 1064-nm laser. This lets the conservator decide about the selection of process parameters depending on the requirements regarding object safety and efficiency criteria. Nevertheless, for careful processing at 532 nm of a longer duration, the energy consumption and also the dose delivered will be roughly the same as that of the faster process at 1064 nm.

The most characteristic data of both dry and wet cleaning monitored acoustically are compared for the 1064-nm laser (Fig. 4b). The signal decrease down to the reference value confirms that for a complete removal of the wet crust, about 10 laser pulses are sufficient, and the applied fluence, as well as the energy deposited, is lower than that required for the dry process by a factor of about 2 and 4, respectively. This is further confirmed by the optical inspection of the cleaning result and clearly indicates the advantages of wet cleaning, in agreement with literature, and also the lower risk of bleaching and alteration of the cleaned object [8,9].

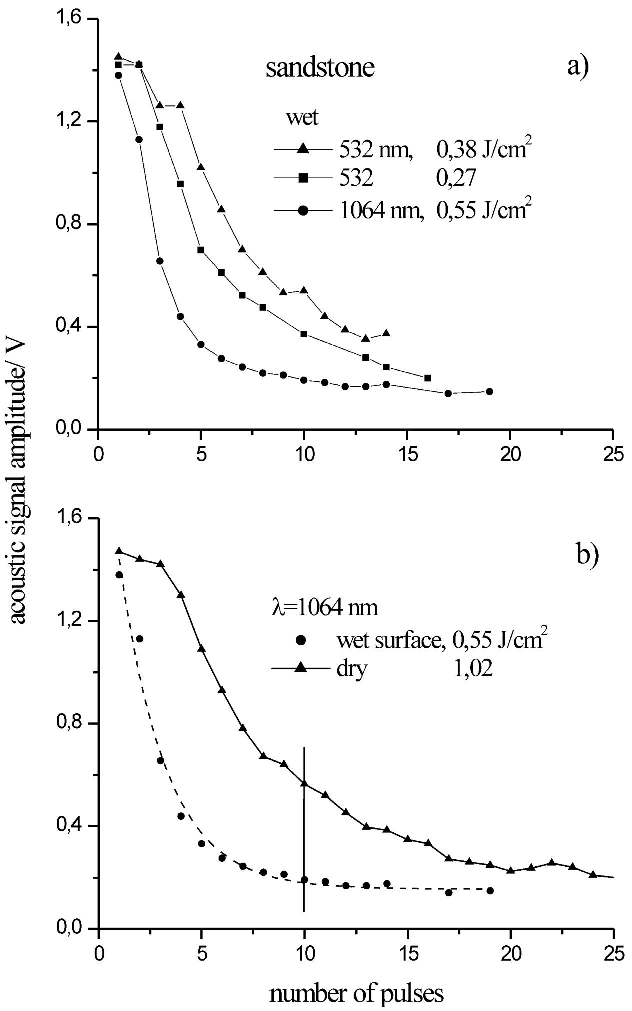

Fig. 4. Dependences of the sound intensity due to pulsed ablation vs. the number of laser pulses at wavelengths of 1064 and 532 nm for the wet crust (a), and comparison of data at 1064 nm for the case of wet and dry surface and optimized laser fluences (b).

3.3. *Sandstone specimen covered by artificial encrustation*

Measurements of sound amplitude dependence on layer thickness were repeated on several areas of the sample in order to minimize the statistical error due to local variations of layer compositions and degree of moistening. Results obtained for the moistened and thoroughly wet samples (1064 nm, 2–3 J cm^{-2}) are shown in Fig. 5a, b. Because of scattering of the experimental data, the values of the sound signal accompanying the material ablation are related to the maximal ones measured for a given layer thickness in the range of 0.2–1.0 mm.

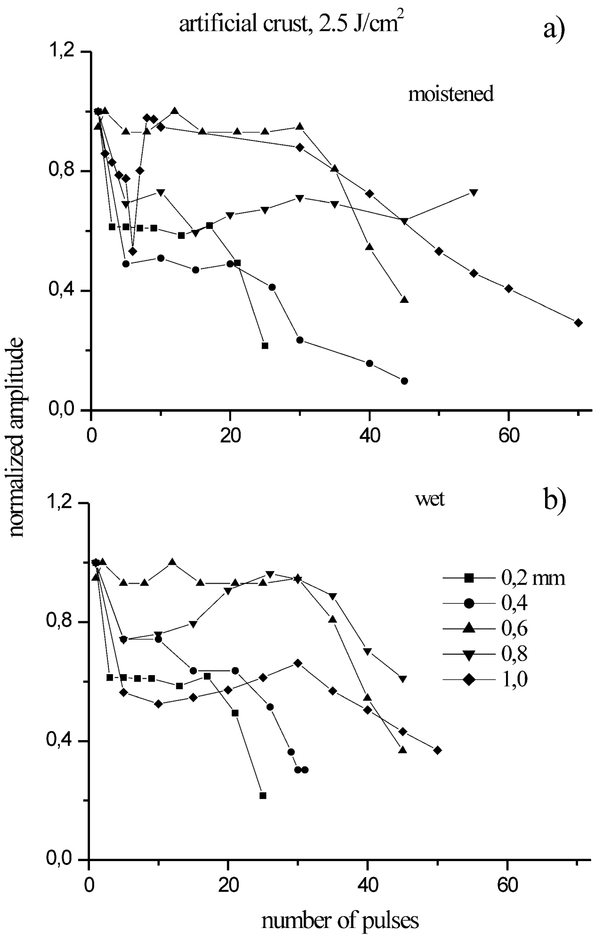

Fig. 5. Same as Figs. 2 and 3, but for the artificial crust of varying layer thickness.

The presence of water does not decrease the initial acoustic signal. In contrast to the original crust, the model material reveals a strong drop of this value by 40–50% for the second laser pulse. A limited regularity of the experimental dependences can be observed only for layers of the lowest thickness, up to 0.4 mm. A decrease of signal with the number of laser pulses occurs in all cases. The larger number of pulses required for the removal of a thicker layer is obvious, and there is no significant difference between results recorded for the cleaning of the slightly moistened and the thoroughly wet samples. The shapes of the experimental dependences are far from that observed for the original crust. In particular, the exponential decay of the sound intensity can be considered only for averaged data. Also, a marked difference occurs between the energy doses applied for removal of the tested layer in both cases. This indicates that the artificial crust is of limited use for the modelling of acoustic monitoring. However, interesting literature data on the analysis of effects, such as blast wave characterization, confirm the advantages of this procedure for understanding the associated physical phenomena [6,7].

3.4. Characterization of the acoustic monitoring

The dashed curve in Fig. 4b represents a numerical fit to the experimental decay of the acoustic signal monitored during removal of the crust according to the relation

$$S(n) = S_{ref} + S\exp(-n/N_0) \quad (1)$$

Here, S_{ref} is the offset signal given by the horizontal asymptote position, which corresponds to the acoustic signal measured experimentally for the stone surface with crust locally removed. The quantity S corresponds to the signal value at the beginning of the cleaning process, and values n and $1/N_0$ represent the process duration and speed (slope of the curve) in units of pulse number, respectively. $1/N_0$ and n can be easily recalculated into the energy dose or time units for a given laser fluence and pulse rate.

The fitting procedure given by Eq. (1) was applied to all data series of Fig. 2, too. However, following the conclusion in Section 3.2, the initial pulses have not been considered, because the acoustic signal measured for them was of limited relevance to the crust removal process. For analysis, the data were normalized with respect to the highest value of $S = S_{max}$ measured in the experiment and became dimensionless:

$$\frac{S(n) - S_{ref}}{S_{max}} = \frac{S}{S_{max}}\exp(-n/N_0) \quad (2)$$

Values of S_{ref}, S and N_0 following from Eq. (2) and plotted vs. the laser fluence of different data series are shown in Fig. 6 a, b, c. For S_{ref}, a relatively narrow band between 8.3% and 11% of S_{max} is observed, which means that the selectivity of the acoustic monitoring in terms of the signal/noise ratio is more than sufficient (see Fig. 6a). This is true for fluences well above the ablation threshold of the crust. It becomes even more pronounced when values of the relative initial amplitude S/S_{max} (see Fig. 6b) and of S_{ref} are compared.

The experimental dependences of S and N_0 on the fluence applied can be well approximated by parabolic curves, which is shown in Fig. 6b, c. In both cases, a clear maximum arises for the same fluence of about 0.45 J cm^{-2}. The acoustic signal amplitude, as well as the reciprocal of N_0 (cleaning speed), decreases to zero with decreasing fluence. This agrees with the limit of the acoustic monitoring for fluences close to the threshold value observed in experiment.

A similar consideration applied to the data characterizing the dry process reveals a broader band of S_{ref} (8–22%) due to the lack of the damping effect (no liquid film on the surface). In this case, the maximal values of the signal detected and cleaning speed are observed for fluences in the range of about 0.8–1.0 J cm^{-2}.

The analysis of experimental data discussed above, when applied to several case studies, allows a comparison of the process parameters related to a given material and obtained

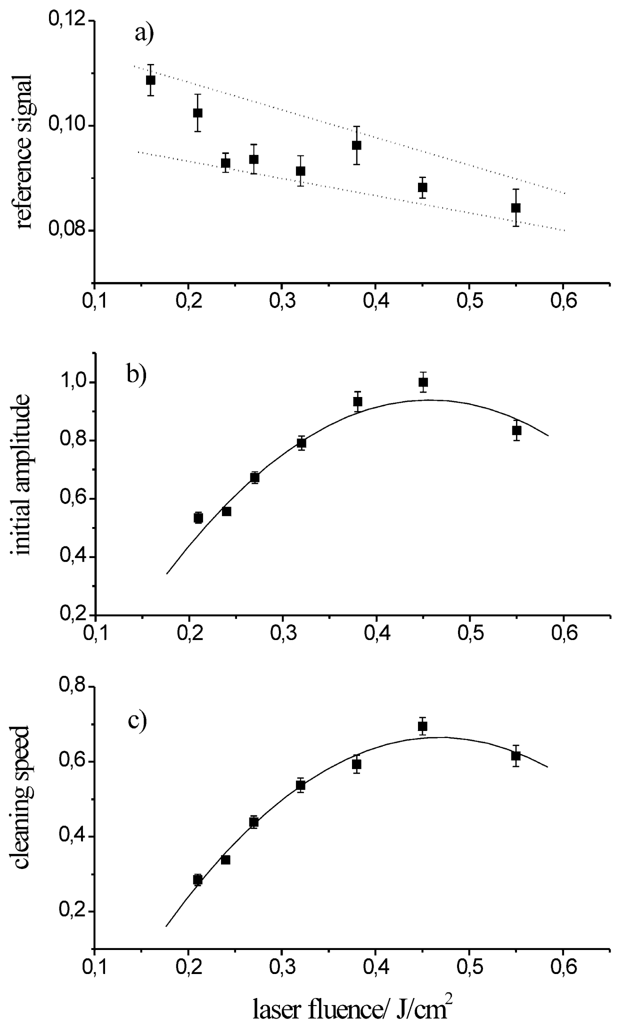

Fig. 6. Values characterizing the acoustic monitoring of pulsed ablation of an original crust from the wet sandstone surface vs. applied laser fluence, Nd:YAG laser, 1064 nm: reference signal (a), initial signal amplitude (b) and cleaning speed (c).

for different laser wavelengths, laser pulse durations and frequencies, and also under various environmental conditions, e.g. wet or dry cleaning. Moreover, it makes possible the selection of the best operating parameters for the laser cleaning of historical stone objects. The collection of such results in the form of a database seems to be a useful tool for the conservator and represents an interesting task for further investigation.

4. Conclusions

The potential of acoustic monitoring for the laser cleaning of monumental sandstone covered by black, grained encrustation and also for specimens with artificial encrustation was investigated experimentally. It was confirmed that the amplitude of the detected snapping sound is directly proportional to the crust thickness and represents a safe and inexpensive method of process monitoring. Results of dry and wet cleaning at 1064 and 532 nm (Nd:YAG laser, 6 ns pulse width) in a broad range of laser fluences of 0.1–2.0 J cm^{-2} were discussed. The artificial crust revealed a drastic decrease of thickness due to several laser pulses, and by prolonged irradiation, a minimum in the signal dependence was observed. The effect was less impressive for thin layers investigated and can be ascribed most probably to the layer drying due to efficient absorption of the laser energy at 1.06 μm. In contrast, results obtained for the originally contaminated, monumental sandstone samples showed a clear, exponential dependence of crust removal on the number of pulses, which was reproduced for several samples. A method allowing for analysis and comparison of data obtained under various experimental conditions was proposed and applied. From consideration of such parameters as the reference signal (no crust), the initial signal value (untreated crust) and the process speed, a clear preference for wet cleaning at a fluence of about 0.45 J cm^{-2} was derived. The optimal cleaning parameters were characterized by maximal values of the process speed and the initial signal amplitude, and were in agreement with a maximum of the detection sensitivity.

The completion of an extended database containing results of other case studies of laser cleaning applied for stone monuments is in progress.

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