Laser surface cleaning of stones and some metal objects

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Dr. Walid K. Hamoudi
Applied Science Department, University of Technology/Baghdad.
E-mail: wjuaini2007@yahoo.com
Dr. Mehdi S. Edan
Ministry of Higher Education & Scientific Research/Baghdad.
Hanan I. Ibrahim1
Applied Science Department, University of Technology/Baghdad.

Abstract

Iron, copper and stone samples were cleaned by Nd: YAG laser using different number of nano laser pulses at variable intensities. Fundamental (1.06 µm) and frequency doubled (0.53 µm) wavelengths cleaning efficiency was tested by measuring the crust and oxide removal rate. A laboratory environmental chamber was built and utilized to study the effect of processing gas on the cleaning process. Surface ref lectivity, SEM and optical microscope investigations indicated the effectiveness of Nd: YAG laser cleaning without damaging the surface. The use of high laser pulse energies helped achieving reasonably good and fast cleaning, whereas low laser energy required larger number of pulses, but ensured safe cleaning. Optimum results were obtained when using the fundamental laser wavelength under O_2 environment.

Keywords: Nd: YAG laser, shock wave, surface cleaning efficiency, ambient gases, optical microscope, SEM.

تنظيف سطوح الاحجار وبعض المعادن بالليزر

الخلاصة

تم تنظيف قطع من الحديد والنحاس والحجر بإستخدام ليزر النيدميوم – ياك النبضي بعد توظيف عدد مختلف من النبضات والشدات الليزرية النانوية. تم اختبار كفاءة الطول الموجي الرئيسي (1.06 µm) والطول الموجي ذو التردد المضاعف (0.53 µm) من خلال قياس معدل ازالة طبقات الاوكسيد والشوائب من على اسطح العينات. تطلب البحث تصنيع حجرة بيئة صناعية لدراسة تأثير نوع الغاز على عملية التنظيف. بعد عملية التنظيف بالليزر عبرت قيم انعكاسية السطح وصور المجهر الالكتروني الماسح وصور المجهر الضوئي عن تميز التنظيف بليزر النيدميوم ياك دون احداث اي تلف لسطح العينة. أوضحت النتائج بأن استخدام طاقات ليزرية عالية قد مكن الحصول على عملية تنظيف مقبولة وسريعة بينما تطلب استخدام طاقات ليزرية صغيرة الى نبضات ليزرية نانوية بعدد اكبر مع ضمان افضل بعدم تأثر سطح المادة. نتجت أفضل عملية تنظيف من أستخدام الطول الموجي الرئيسي (1.06 µm) لليزر النيدميوم – ياك النبضي.

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

INTRODUCTION

Artifacts of ancient civilizations are vital for the historical and cultural identity of each country [1, 2]. Aging and environmental changes make the materials of these artifacts unstable and falling apart and damage their identities [3-5]. Choosing the appropriate safe technique depends on the original material being treated and the crust [6, 7]. Conventional micro-blasting, air-abrasive, chemical and steam cleaning without stringent care could damage the underlying surface [8, 9]. Laser cleaning is based on selective sputtering of optically absorbing pollutants; first adopted by repairs project in 1993 at the Cathedral of Amiens [10-12]. It is effective, controllable, environmentally friendly and flexible; more than conventional techniques [13-17]. High peak power pulsed lasers are utilized to remove surface stains and weathering effects from sculptures, coins, marble, granite, frescos, paintings, paper and textiles [8, 18]. It is also used to remove pollutants or corrosion layers from a wide range of metals and stones [15]. The interaction of laser radiation with materials depends on laser and materials properties [19, 20]. The absorbed laser energy by the material depends on the wavelength of the laser and the spectral absorptivity of the material. This heat is diffused into the material according to Fourier's second law of heat transfer and radiates from the surface at the same time [14]. A localized rise in temperature on the surface of the material leads to melting and vaporization and finally results in the plasma formation with a temperature up to several thousand degrees [6]. This causes thermal expansion and the generation of mechanical shock waves and inertial force in the contaminations by the end of pulse. This shock wave propagates through the material, breaks it down and causes the dispersal of particles of different sizes [8]. Laser induced shock waves have shown successful results in many applications such as; industrial, medical, scientific and cleaning of artifacts and preservations. Laser is localized and can be employed in out-of-the-way places. In addition, it is automated, non-contact and much faster than conventional methods. In 1998, Kearns et al. [21] showed a successful removal of copper oxide above specific energy fluence threshold, by using 1064 nm, 532 nm and 266 nm laser wavelengths. Lower laser fluencies caused surface melting while higher values induced oxide removal. In 2000, J. Lee, et al. [15] achieved higher copper oxide cleaning efficiency when shining the laser at a glancing angle to the surface. In 2006, L. Bartoli, et al. [22] showed that short laser pulses are more effective than long duration ones in the cleaning of real and simulated crusts from marble. In the same year, M. Jasi et al. [16] used 0.5 J/cm^2 fluence pulsed Nd: YAG laser operating at 1064nm to completely remove 100–200 μm thick porous encrustation after 12–18 laser pulses. In 2013, S. Pozoa, et al. [26] investigated the removal of sulphate-rich black crusts on granite using 6-10 ns, 10 Hz, Nd: YAG laser; operating at 266 nm, 355 nm, 532 nm harmonics and fundamental 1064 nm wavelengths. Their indicated efficient cleaning results when using the longer wavelength (1064 nm). In the present study, Nd: YAG laser, operating at fundamental (1064nm) and second harmonic frequency (532nm), was utilized to find the optimum laser and ambient parameters required to efficiently clean environmentally affected stones and metals without causing any damage. The objective is to have safe and efficient cleaning method in order to maintain the artistic and historic values of artifacts.

Experiment

Oxidized iron plates, Oxidized copper plates and simulated crust on marble samples were laser cleaned by using 7 ns, Q-Switched Nd: YAG laser (type

HUAFEI). A controlled gas flow system was built and utilized. 100X optical microscope (Kross, Germany) and (Tescan VEGA ii, Czech) Scanning electron microscope (SEM) were Employed to study the morphology and microstructure of the treated samples. 2mW He-Ne laser, power meter and positive lens were finally used to investigate the surface reflectivity, i.e. clearness achieved after each cleaning protocol. Laser cleaning of iron and copper oxides, as well as, thick simulated crust on marble was performed; using Nd: YAG laser system operating at 1064 nm and 530 nm wavelengths with different intensities and number of pulses. The simulated crust composition was prepared by mixing 49.52% ($CaSO_4.H_2O$), 0.5% (Fe_2O_3), 1% (carbon) and 48.98% water. The marble samples were exposed to different laser and environmental (CO_2, N_2, Ar_2, O_2) gas conditions. The cleaning efficiency and removal depth were calculated for each set of treating parameters.

Laser cleaning of metals

Figure [1] shows the difference between cleaning of oxidized iron plate by laser and by chemicals. Chemical cleaning is an uncontrolled process in which effective parameters, such as, concentration, reaction time, diffusion of chemicals into the substrate and the environment temperature, could not be adjusted for optimum results [18]. Figure (1-C) shows an excessive damage of the iron plate when cleaned by diluted (1:10) HF acid, whereas, better results were obtained with Nd: YAG laser cleaning with no substrate damage; figure (1-D). When minimum laser intensity is used for cleaning a 0.4mm thick simulated iron oxide and crust, 98 pulses were needed to fully clean (0.87 mm^2) from the surface. The crust thickness decreased with the increasing number of laser pulses using constant intensity of ($3.36x10^{10}$ W/cm^2). With higher laser intensities, smaller number of pulses cleaned the crust effectively, as depicted in table (1).

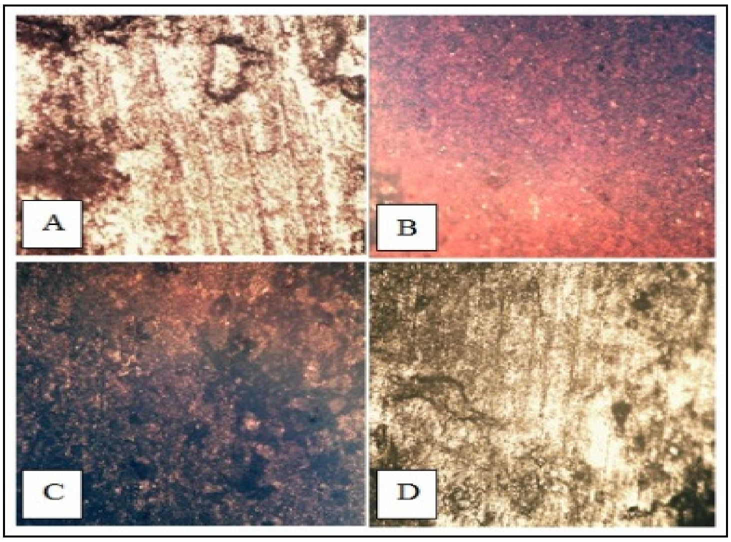


Figure (1) Microscopic top view of iron plate (100X): (A) before oxidation, (B) after oxidation, (C) after cleaning with diluted HF acid and (D) after cleaning with 1064nm laser using 4 pulses, each of 6.12 x $10^{10}$$W/cm^2$ intensity.

The cleaning process was investigated by an optical microscope for different laser intensities. The topographic surface image of the oxidized iron plate shows an enhanced surface clearness at higher laser intensities (higher laser energy); figure (2). This however, could endanger the surface.

Table (1) Number of cleaning laser pulses at different laser intensities.

Laser intensity W/cm^2	Number of cleaning laser pulses
$3.36x10^{10}$	98
$4.89x10^{10}$	84
$6.12x10^{10}$	39
$8.25x10^{10}$	29
$9.17x10^{10}$	16

Larger number of lower intensity laser pulses allowed safer removal rate of oxide at moderate rate, as shown in figure (3). Excessive laser energy induces some damage to the underlying substrate while lower laser energy can keep the cleaning conditions just above the ablation threshold and ensures safe cleaning. The use of laser energy below the ablation threshold caused blackening of the surface due to the melting of the oxide layer [21]. Laser etching of refractive substrates takes place at much faster rate than laser etching of pollutants. This requires very careful control on the process to avoid substrate damage. Pollutants on high reflectivity metals, on the other hand, are safer to remove by nanosecond 1064 nm laser pulses since it avoids the thermal conductivity role on transferring the energy into deeper layers [23].

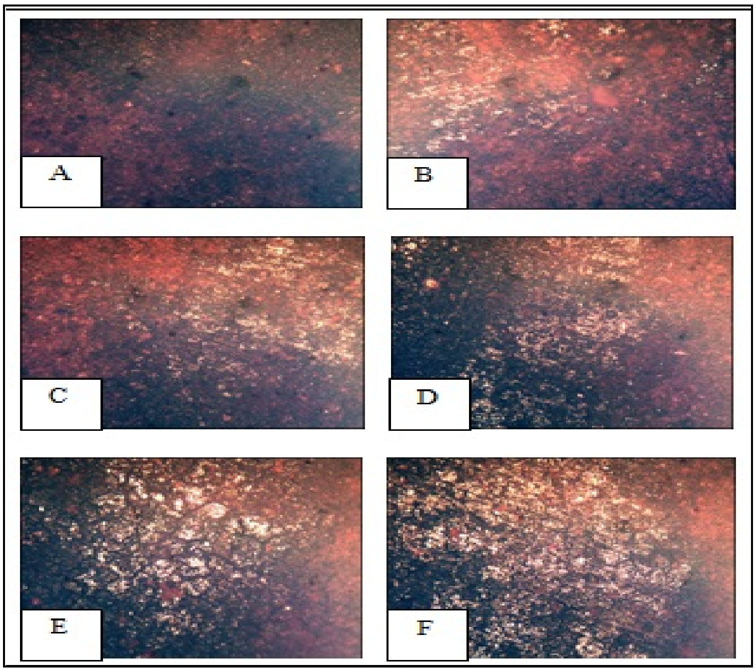


Figure (2) Microscopic top view of iron plate cleaned with single laser pulse at different intensities (100X), A: untreated sample, (B: 3.36, C: 4.89, D: 6.12, E: 8.25, F: 9.17) x1010W/cm2).

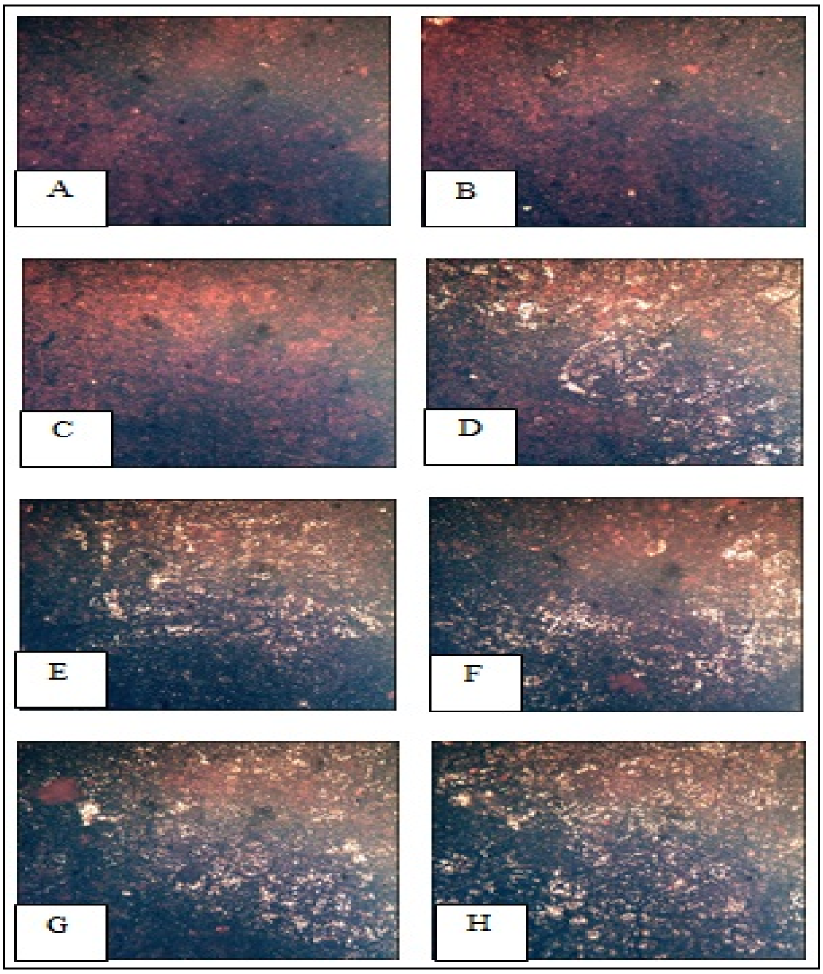


Figure (3): Microscopic top view of iron plate cleaned with 3.36x10^{10}W/cm^2 intensity using 1, 2, 3, 4, 5, 6, 7 and 8 laser pulses (100X).

To make a real test, a Jordanian copper coin was cleaned with different laser intensities. Optimum cleaning results was achieved at 10 pulses of 4.89 x10^{10} W/cm^2 intensity using 1064nm Nd: YAG laser with 50% pulse overlap. The treated part of the copper coin was clear from crust and showed bright surface color when compared with the un-treated part as shown in figure (4).

Figure (4): Laser cleaning of Jordanian copper coin using 4.89x1010 W/cm2, laser intensity.

Cleaned surface reflectivity was used as a measure of the cleaning efficiency. This reflectivity was increasing with the laser intensities, as shown in figure (5). Higher intensities were more effective on oxide layers and required smaller number of pulses. Maximum reflectivity of 6.944% (cleaning efficiency) was achieved at 9.17 x10^{10}W/cm^2 pulse intensity. This result is close to the reflectivity of the original iron substrate before oxidation (8.61%). Figure (5) also illustrates a relation between surface reflectivity and pulses number. The behavior quickly became linear where additional pulses did not change the cleaned surface reflectivity. This is attributed to the self -limiting property of laser cleaning of metal surfaces which prevents the substrate from damage.

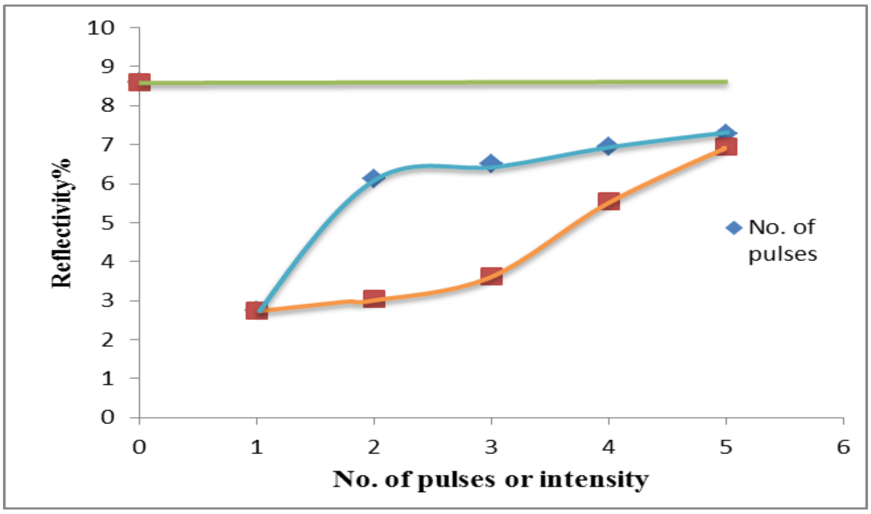


Figure (5): Reflectivity at different laser intensities (3.36, 4.89, 6.12, 8.25 and 9.17) x10^{10}W/cm^2) using a single laser pulse.

Figure (6) shows the effect of laser intensity and the number of pulses on the crust removal depth. Higher laser intensity was more effective on oxide layers and required smaller number of pulses [24]. The figure shows a limit for removing the crust after certain number of pulses due to the diminishing laser energy when penetrating deeper thickness of crust.

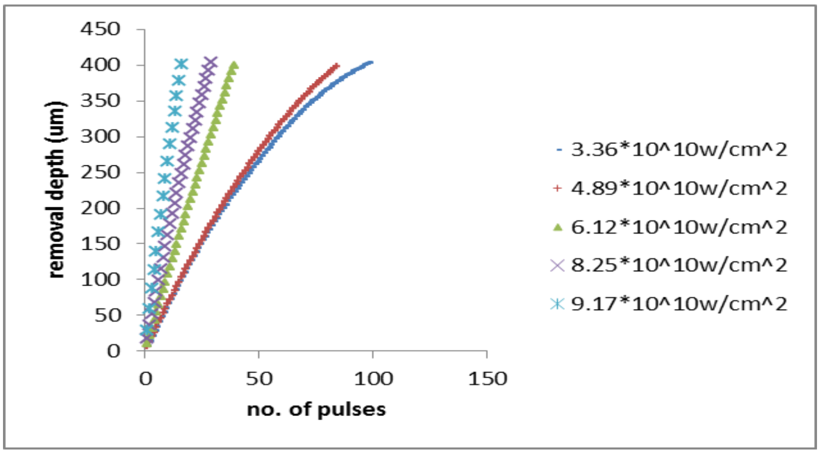


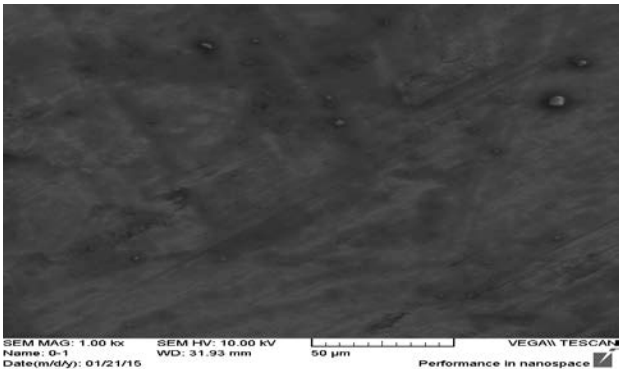
Figure (6) Crust removal depth from iron plate versus number of pulses and laser intensities.

The effect of laser wavelength was investigated by scanning electron microscopes and presented in figure (7). Four pulses from Two Nd: YAG laser wavelengths; the fundamental 1064nm and its second harmonic (SHG) 530nm at intensity level of $6.12x10^{10}w/cm^2$ were used. The results of cleaning iron plate revealed the superiority of the 1064 nm over the 532 nm. The cleaned surface was shiny with clear appearances, and very close to the original surface before oxidation. The use of SHG 532nm wavelength resulted in partial cleaning with some changes in the microstructural morphology. The SEM micrographs showed similar surface morphology as that of the original (the lower part on the right of figure (8-B). This indicates an efficient laser energy absorption by the crust and not by the metal; a good finding that ensures safe cleaning without damage.

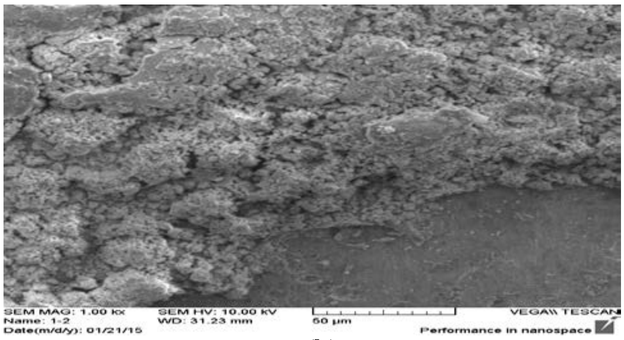
Laser cleaning of Stones

Simulation crust cleaning by (1064nm) wavelength was very effective in eliminating the $CaCO_3$ from the surface [25]. The images of the cleaned stone surfaces; examined by optical microscope, showed better cleaning results with oxygen or nitrogen ambient gases; figure (8-C&E). The figure also shows cross-sectional views of decreased crust after laser illumination. The use of ambient oxygen permitted very good cleaning and better than other gases, due to its smaller ionization energy (12.1 eV) and higher thermal conductivity (63.64cal/sec.cm.c^o $x10^6$ [16]. Part of the laser beam energy was used to burn the oxygen in an exothermal reaction

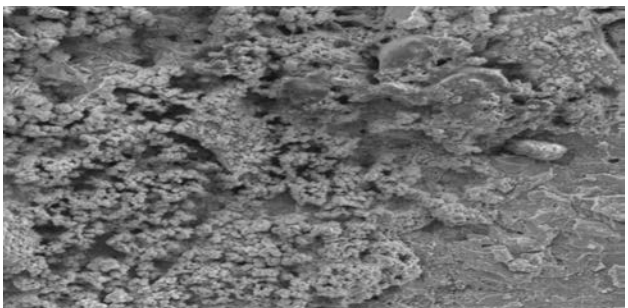
Which increased the thermal energy at the surface. This has ensured an efficient removal of the crust without affecting the substrate. The use of CO_2 ambient showed lower degree of crust removal. This is attributed to its low thermal conductivity (39.67cal/sec.cm.c^o x10^6) and high ionization energy (13.8 eV). The nitrogen gas induced good cleaning due to its high thermal conductivity (62.40cal/sec.cm.c^o x10^6) and good laser-crust coupling. Finally, the use of argon ambient produced the smallest decrease in crust thickness because of its higher ionization energy (15.8 eV) and low thermal conductivity (42.57cal/sec.cm.c^{o}x10^6). 2mW, He: Ne laser and a power meter were used to measure surface reflectivity. Comparable reflectivity (2.75%) of the cleaned surface with that of the original one (3.15%) was achieved when using 9.17 x 10^{10} W/cm^2, intensity under O_2. Figure (9) and Table (2) show the reflectivity results obtained for all ambient gases.



(a)

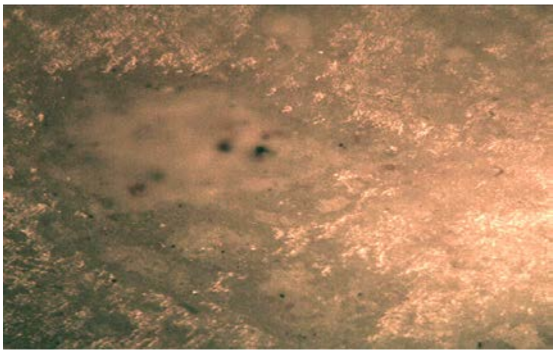


(b)



(C)

Figure (7) SEM images of iron plate A: reference untreated sample B: cleaned with four 1064 nm laser pulses and C: cleaned with four 532 nm laser pulses (laser intensity = 6.12x10^{10} W/cm^2).



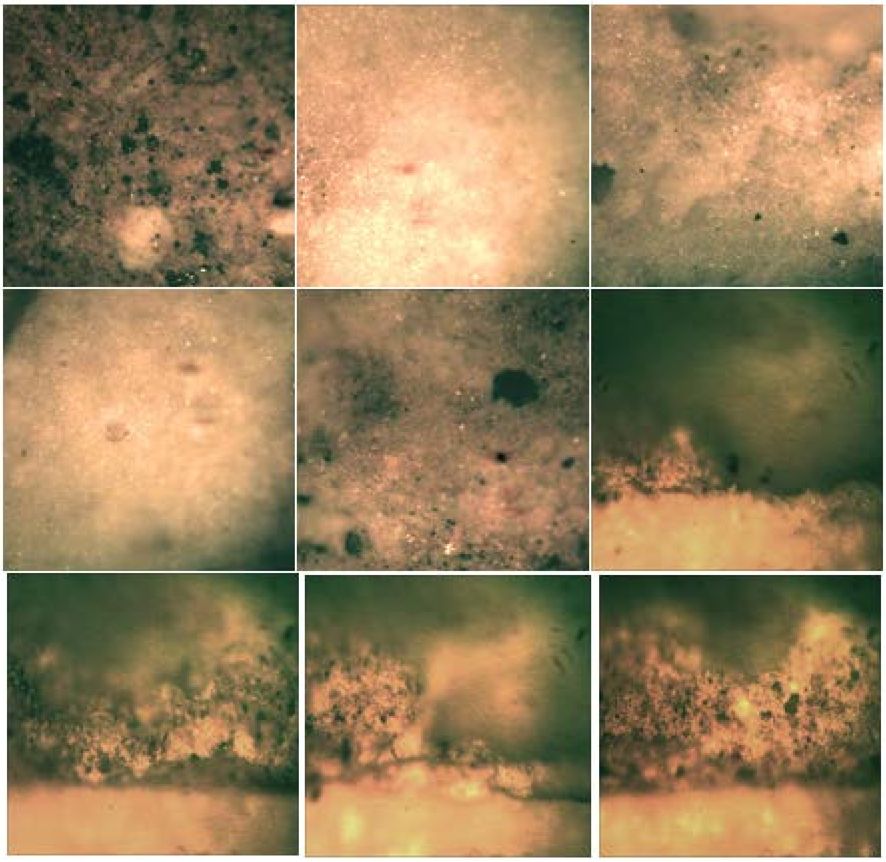


Figure (8) Microscopic top view images of stones (100 X) using 4; 6.12 x10^{10} W/cm^2 intensity pulses and 0.1 mm crust thickness, A: crusted sample, B: reference sample, C: O_2 ambient, D: CO_2 ambient, E: N_2 ambient, F: Ar_2 ambient, G: cross-sectional image under O_2 ambient, H: cross-sectional image under CO_2 ambient and I: cross-sectional image under Ar_2 ambient.

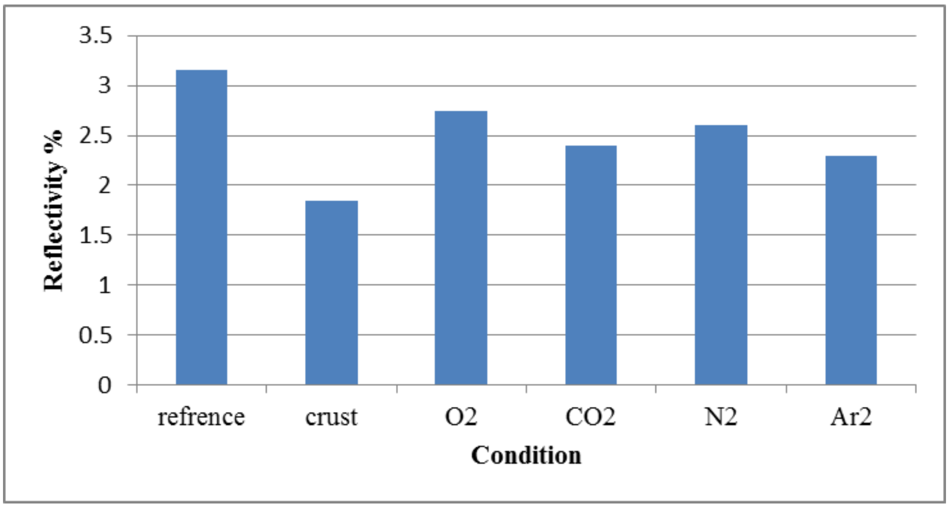


Figure (9) Reflectivity of stone substrates for different conditions: reference, crust before cleaning, and (O2, CO2, N2, Ar2) gases presence

Table (2) Reflectivity results of stones.

Sample	**Reflectivity % at λ = 665 nm**
crust	1.85
Untreated sample	3.15
Cleaned under O_2	2.75
Cleaned under CO_2	2.4
Cleaned under N_2	2.6
Cleaned under Ar_2	2.3

Conclusion

For iron plate, maximum reflectivity (optimum cleaning efficiency) of 6.944% was achieved at 9.17 $x10^{10}W/cm^2$ intensity; which is close to that of the original iron plate before oxidation (8.61%). For laser cleaning of stones, the optimum intensity needed to accomplish a good job was 6.12 $x10^{10}$ W/cm^2. High laser pulse energy enhanced the clearness of both iron and stone, but too high values exposed the substrates to physical damage. Large number of low energy laser pulses allowed safer cleaning. The fundamental Nd: YAG laser (1064nm) wavelength was more effective and safer cleaning tool than the frequency doubled (532 nm) wavelength. The use of O_2 ambient gas permitted better stone cleaning than with CO_2, N_2 and Ar gases.

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