Laser cleaning of *Prestige* tanker oil spill on coastal rocks controlled by spectrochemical analysis


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Abstract

The potential of laser technology for controlled clean-up and analysis of *Prestige* tanker oil spill from coastal rocks is examined. Some of the massive cleaning methods cause more damage on the environment than they want to prevent. Laser treatment offers advantages with respect to these techniques such as the absence of additional residues and a minimal damage to the underlying substrate material. For these reasons, laser cleaning is presented as an alternative or complementary method in spills response available for minimizing their impact on the environment and human health.

Test results of the yield of the laser cleaning process performed by a Nd:YAG laser emitting at two wavelengths are presented for various types of rocks polluted by the spill found on the north Galician coast. The laser cleaning process is controlled by the spectral analysis of the emission from the laser-produced plasma in order to avoid damage to the original rock surface. In order to provide complementary data, a morphological and compositional comparison of polluted and cleaned pieces has been performed by scanning electron microscopy and energy dispersive X-ray spectroscopy.

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1. Introduction

The oil spill from the *Prestige* tanker has devastated large sections of the Galician coastline in Spain since November 2002 [1]. This environmental and economical disaster has demanded the development of fast, controlled and environmentally harmless cleaning techniques for fuel removal. Classical mechanical (water stripping) and chemical (dispersants) procedures for rocks cleaning are difficult to control and generate waste and debris that require complementary techniques for their removal [2–4]. On the other hand, while chemical agents can be toxic, water washing can cause the sterilization of rocks by the elimination of sediments and nutrients. Therefore, despite the final clean aspect of the rocks, these methods may cause more environmental damage than fuel by itself and are not recommended in some contaminated zones that are specially delicate. New technologies have been developed, including bioremediation, which uses microorganisms to breakdown the hydrocarbons into less harmful compounds, but their ecological impact and applicability are still under study [5].

Laser technology described in this paper is proposed for the first time as an alternative or complementary technique for the clean-up of fuel spill from rocks in specific zones of the coast where classical cleaning procedures are too aggressive and damaging due to the waste generated or to the uncontrolled cleaning process itself. This can be the case in some zones of harbours, docks and natural protective spaces that require a more precise and harmless treatment or where the presence of waste or chemical agents is not acceptable. Another part of the Galician coast that cannot be cleaned by mechanical methods but requires a “softer” method such as that proposed here is the so-called “Museum of the German”, an open-air beach museum of stone, wooden and bone sculptures situated in the Galician fishing village of Camelle and constructed by a German hermit. This place had been a popular tourist attraction for those visiting the Galician coast until it was damaged by the oil spill.
Laser radiation has been reported as a powerful tool for the removal of surface contaminants and the analysis of a wide variety of substrates in both industrial [6–8] and cultural applications [9]. In comparison with other cleaning techniques, laser methodology can offer the advantages of automation [10,11], adaptation to portable units and, most importantly, a high degree of on-line control through a variety of in situ detection laser-based analytical techniques, which allows the complete selective removal of surface contamination with minimal damage to the underlying substrate material. Furthermore, the laser technique is an environment-friendly cleaning tool since no contact or additives are necessary and almost no toxic wastes are produced during the cleaning process. In addition, controlled laser cleaning can be applied to large areas, including building fronts [11–13], walls [14], sculptures [10,15] and aircraft [16].

The on-line monitoring and in situ control of material removal at all stages of laser cleaning can be achieved by using laser-induced plasma spectroscopy (LIPS) [10,11,17–19]. This method of control relies on the spectral analysis of the emission from the plasma produced during laser ablation. In this sense, when a pulsed laser beam is focused onto the sample surface, it induces not only the ejection and vaporization of material from the sample surface, but also the formation of a plasma which emits light at wavelengths characteristic of the elemental composition of the removed layer. Therefore, the analysis of the emission spectra provides detailed information about surface composition at each cleaning pulse, that is, the in-depth compositional profile of the sample. This process control guarantees the removal of the unwanted superficial material without damaging the original surface, based on the different elemental composition of the removed layer. In addition, the coupling of this spectroscopic technique to the cleaning process provides important information about the optimal experimental conditions to be selected for achieving an adequate cleaning procedure.

In this work, a laser-based methodology is tested for controlled cleaning of Prestige oil spill residues from rocks for its application to some zones of Galician coast that require special treatment. The results show the capability of LIPS for monitoring and on-line controlling the laser cleaning process. In addition, a qualitative elemental analysis of both fuel oil and rocks performed by LIPS is compared to that achieved by scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX).

2. Experimental

Fuel cleaning from rocks was performed by using a Q-switched Nd–YAG laser source (Quantel, model Brilliant B) pulse width 6 ns (FWHM), beam diameter 9 mm, operating at a pulse repetition rate of 10 Hz at two wavelengths, 1064 and 355 nm, fundamental and third harmonic, respectively. According to the laser wavelength used, the energy output was 900 mJ or 200 mJ per pulse. In some of the experiments where the energy density was not sufficient to perform an adequate cleaning process, the laser beam was focused using a plano-convex quartz lens (\(f = 300\) mm). Experimental conditions resulted in an energy density range from 1.2 to 80 J cm\(^{-2}\).

The cleaning process was monitored by recording emission spectra obtained from the laser produced plasma. For this purpose, the plasma emission was collected with a plano-convex quartz lens (\(f = 150\) mm) and focused into a 125 mm focal length spectrograph (Oriel, model 77400) fitted with a micrometer driven, variable width slit, fixed at 40 \(\mu\)m, and a 1200 grooves \(\text{mm}^{-1}\) grating. The spectrograph was equipped with a ICCD detector (Andor, model DH 2802) provided with a 512 × 512 matrix of pixels, an active area of 12.3 mm × 12.3 mm and a spectral range from 180 to 850 nm. The ICCD was controlled with Andor MCD software, working in full vertical binning readout mode with background correction. With the 1200 grooves \(\text{mm}^{-1}\) grating, spectral coverage of around 80 nm was collected in each spectrum. ICCD time-gating control was carried out by a delay generator (Stanford, model DG-535) triggered by a TTL signal from the Q-switch output of the laser. Plasma emission was acquired over 500 ns, delayed by 0 and 500 ns from the laser firing in order to favour the observation of ionic emission lines and atomic emission lines, respectively.

Pieces (rocks fragments and stones) with different humidity stages and covered by different fuel thicknesses from the Galician coast have been irradiated in air at ambient temperature and pressure. It should be noted that the oil transported by the Prestige was a heavy fuel, used for two kinds of applications: industrial combustion and supplying ships propelled by powerful, slow diesel engines. The fuel is a very viscous water-insoluble product, basically composed of saturated hydrocarbons, resins, naphthalenes and polycyclic aromatic hydrocarbons (fuel oil no. 6) [20].

Owing to the rugged topography of the pieces, samples were situated in \(X–Y–Z\) stages and an alignment system consisting of two He–Ne lasers was used to help in sample positioning in terms of laser focal point situation, collection alignment and point-to-point clean-up.

3. Results and discussion

In a preliminary stage, different rock fragments and stones free of contamination as well as the fuel crust from polluted pieces were analyzed by LIPS to select the optimum spectral window for detection. For this purpose, emission spectra from the plasma generated when irradiating the samples with the pulsed laser beam were collected from 240 to 590 nm. The major differences in elemental composition between the fuel layer and the non-contaminated material were observed in the spectral window from 240 to 322 nm. Therefore, only the analysis results in that spectral region are presented here. The NIST atomic spectral database was
used for the assignment of the emission lines [21]. The LIP spectra of CaCO₃, SiO₂, Mg(NO₃)₂, graphite and metallic Fe, Ti and Al were used as references. The experimental LIP spectra of rock and fuel are shown in Fig. 1. As observed, fuel-polluted and non-contaminated rock zones had different compositions. Si and Al were present in the original rock, while C, Mg and Ca were detected in the fuel crust. In addition, the Na (I) 588.995 nm emission line has been also detected in both fuel and rock. Although only the most representative spectra are presented in Fig. 1, several rock types were analyzed, observing variations in the proportion of Si and Al and the presence of Fe, Mg and Ti in some rock phases, but in all cases the LIP spectrum differs substantially to that of the fuel.

It should be noted that the compositional results are qualitative. To corroborate the elemental analysis performed by LIPS, both rock and fuel layers were analyzed by SEM–EDX. Secondary electron micrographs of fuel-polluted and non-contaminated zones of the same rock fragment are shown in Fig. 2. The images reveal topographic differences in both materials. In particular, the fuel crust presents a doughy appearance with numerous cracks in contrast to the porous structure of rock. It should be noted that this crack appearance of the crust decreases with the increase of fuel humidity grade, as was observed by comparison of SEM micrographs of different samples. Fig. 3 shows EDX spectra of the zones imaged in Fig. 2. From the observation of these spectra it can be deduced that O and Na are present in both areas, oil polluted and non-contaminated; Si and Al are located in rock with a minority presence of K and Fe, while the fuel layer consists of C, Mg, Ca, Cl and S. These results are in full agreement with those obtained using LIPS. It should be noted that the more intense emission lines of K, Cl and S were out of the spectral range considered in the present LIPS study. The presence of a weak signal of Si in the EDX spectrum of fuel may be the result of a slight contribution of the underlying rock material to the analysis due to the long-range depth of
Having established the compositional differences of fuel layer and rocks for monitoring purposes, the laser cleaning process was tested. The procedure consisted of irradiating the polluted pieces by means of the pulsed laser beam to generate energy densities able to remove layers or particles of fuel at each laser shot. Fig. 4 shows part of the spot sequence as the result of firing 15 laser shots at 1064 nm over a single position of the surface of a fuel-contaminated rock fragment. In the figure, the dark areas correspond to the fuel layer while the brightest areas correspond to the underlying rock surface that has been partially exposed by the impact of the laser beam. As observed in the photographs, each laser shot induces a cleaner rock surface, indicating the availability of laser ablation for fuel crust cleaning from coastal rocks.

It has to be pointed out that the number of pulses required to reach the original rock surface varied from one region of the sample to another due to differences in fuel layer thickness. For this reason, coupling of an on-line diagnostic technique to the cleaning process was crucial for avoiding overcleaning. The control of material removal during laser cleaning was achieved by LIPS. In this respect, when the laser was fired repetitively over the same position of the sample surface, depth-related spectra were obtained by monitoring the laser-induced plasma emission from each laser shot. An example is shown in Fig. 5, where the first, 15th, 30th and 45th LIP spectra corresponding to a sequence of laser shots over a single position of the fuel crust have been plotted. The upper spectrum, corresponding to the first laser shot, presents characteristic emission lines for C, Mg and Ca, indicating that the fuel layer is being ablated. However, a significant decrease in C and Mg emission intensities is observed along with the gradual appearance of Si and Al peaks in the spectra related to 15th and 30th laser shots. At the bottom, the spectrum acquired after 45 laser shots exhibits the presence of Si and Al while C, Mg and Ca are
absent. This observation indicates that the underlying rock surface has been reached and the fuel layer has been eliminated.

As shown, the collected spectra are characteristic of the composition of the material expelled at each cleaning stage, so the compositional information obtained by LIPS allows it to be established in real time if the cleaning process is finished. In this respect, monitoring the intensity development of some emission lines can be used as an indicator of the extent of the cleaning process. In particular, the progresses of C (I) 247.856 nm and Si (I) 288.158 nm emission intensities along the sequence of spectra partially plotted in Fig. 5 are shown in Fig. 6. As expected, the C intensity decreases in contrast to the Si intensity that grows with the number of laser pulses until the signal stabilizes. These behaviours are in agreement with fuel disappearance and rock uncovering. From the plots of Fig. 6, it can be deduced that the fuel layer has been completely eliminated after 45 pulses in depth. In that point, the cleaning process could be stopped but, in this case, more pulses were fired at the same position for a better understanding of signal development. The results demonstrate the capability of LIPS for exact and precise on-line control of the cleaning process by monitoring the emission signal development.

The cleaning process was repeated in adjacent positions by moving the sample step by step in the X and Y directions, resulting in a cleaned area. Fig. 7 shows a fuel-polluted stone before and after the cleaning of a portion of the contaminated surface. Black areas correspond to fuel crust while grey areas correspond to the underlying rock surface exposed after the laser treatment. For achieving this laser stripping process, an average of 30 pulses was required at each position in the sample. The process was monitored by LIPS to control the extent of the cleaning treatment, thus removing the unwanted fuel material without actually affecting the original stone surface.

Further studies are being carried out to evaluate the effect of experimental parameters on cleaning yield and establish a cleaning protocol for automatic control of the laser stripping process.
Fig. 7. Photograph of a fuel-polluted stone: (a) before laser treatment; (b) after laser cleaning of the right side of the stone surface. Laser wavelength: 1064 nm, laser repetition rate: 10 Hz, average laser shots per position: 30, cleaned area: 49 mm × 21 mm.

4. Conclusions

Laser technology has been successfully applied to oil spill cleaning from coastal rock surface. The results suggest laser treatment as a good alternative or complementary technique to traditional cleaning methods in oil spill contingency procedures in some zones. In addition, LIPS can not only provide information about fuel composition but also be used as a tool for an efficient on-line control at all stages of laser cleaning by monitoring composition changes of the removed material. This control capability is especially valuable due to the variability of fuel layer thickness over the entire rock surface and allows the selective removal of fuel polluting layers with high precision without altering the original rock surface.

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References