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Thermal effects induced by laser ablation in non-homogeneous limestone covered by an impurity layer

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ABSTRACT

This paper reports preliminary results concerning thermal effects induced by urban/industrial air pollutants deposited on a limestone rock when heated by pulsed laser in the cleaning process. The process of laser cleaning treatment of the crust is simulated using COMSOL Multiphysics 4.4, finite element analysis software. Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy and Laser Induced Breakdown Spectroscopy techniques have been used to analyze the chemical composition of the samples. Two elements found as being present into the dust and in the crust, such as iron and magnesium particles are used for simulation in COMSOL. Therefore, the profiles heat evolutions on the crust surface and inside limestone are obtained as thermal interactions between the three components (iron, magnesium and limestone), simulating the non-homogeneous materials. It has been observed that iron impurities caused by the dust deposition may damage the limestone through a process of overheating, as a consequence of a high thermal conduction phenomenon, recorded for the region with iron impurities and sizes of micrometric order are localized. The thermal contact between the three components results in plots that reflect their thermal interactions.

1. Introduction

The atmosphere pollution affects the old buildings, monuments and other civil constructions (usually made of limestone materials) by forming on their surface of a crust with air pollutants (due to the gravity deposition of different aerosols) that, in time, changes their aspect and color (due to chemical reactions) and determines their degradation (due to physical processes such as moisture) [1,2]. Laser ablation is one of the advanced methods used for the cleaning of the deposited crust [2]. The crust chemical compositions depend on the pollutants existing in the atmosphere (urban and industrial ones) and thus call for particular control and selectivity. In order to make an evaluation of the laser parameters for ablating the undesired deposition, preserving at the same time the substrate [3], we choose to simulate first the laser effects using the finite element method (FEM) with COMSOL Multiphysics software. In the typical experimental method, the optimum laser parameters could be found after certain number of trials that require long time until the best option is determined and a significant number of samples. By contrary, the advantage of the simulation in COMSOL is that reduces the number of trials and samples and offers information about the temperature achieved on the crust but also inside the material. Thus, it provides information on the damage threshold of the material due to thermal effects and possible chemical reactions that will be considered when laser parameters are chosen for experimental work and subsequent practical cleaning. COMSOL Multiphysics simulations reported on laser irradiation proved to be in good accordance with experimental data [4–6].

The main aim of our work is to set-up the basis of a method of simulation that will allow further development for evaluating laser parameters when non-homogenous layer pulsed laser irradiated is studied. For computational reasons, a simplified model is used consisting of a layer deposited on a limestone support. The

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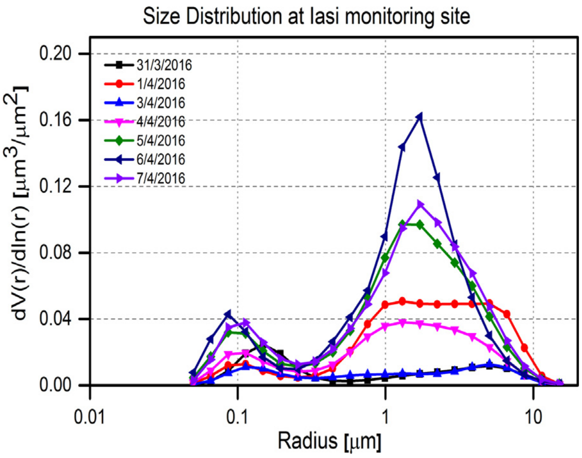

Fig. 1. IASI LOASL – AERONET data, Aerosol particle size distribution.

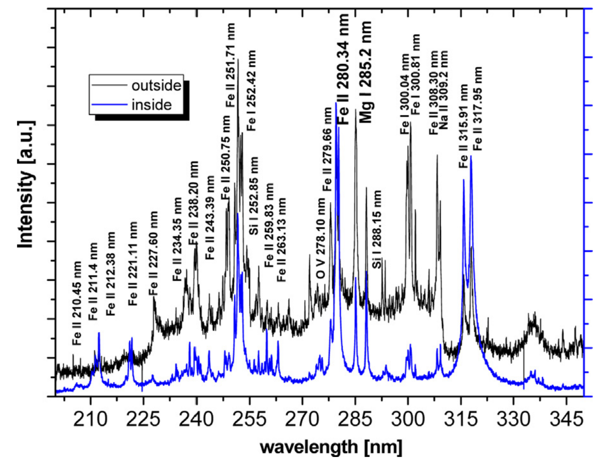

Fig. 2. Limestone rock spectral composition – by LIBS technique.

layer is considered as being made of two materials (iron and magnesium) in contact. This representation is preferred because of the high thermal properties of the two elements, especially iron, and the thermal effects can be studied at limit conditions.

2. Materials and methods

Following the aim of our study, we started with the analysis of the aerosols that caused the crust formation and analysis of the crust and interior of the rocks. A number of elements present in the urban aerosols, mostly of industrial provenience, including also Saharan aerosols have also been found in the crust deposited.

2.1. Aerosols analysis

The information about aerosols analysis was retrieved from Aerosol Robotic Network (AERONET) [14], from IASI LOASL monitoring site (Latitude: 47.193061 North, Longitude: 27.555561 East, Elevation: 175.0 m, station of Romanian Atmospheric research 3D Observatory – RADO) for several days (March 31, 2016 to April 7, 2016) [7–13]. Depending on the concentration of Saharan dust from tropospheric column and urban-industrial aerosols type, the fraction of large particles (coarse mode aerosols with radius greater as 1 μm) was ranging, being higher in the total column of atmosphere on the April 6th, 2016 (Fig. 1).

2.2. Crust and rock elemental composition analysis

The crust elemental composition analysis was performed using Laser-Induced Breakdown Spectroscopy (LIBS) with an Acton 2750i high resolution spectrometer (750 mm focal length) coupled with a Roper Scientific PIMAX3 ICCD camera 1024 × 1024 pixels with a minimum gate time of 2 ns. The obtained results were compared with SEM/EDX (Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy, Vega II LSH – Tescan, coupled Quantax QX2 – Bruker – Roentec) investigations [15–18].

Analyzed samples are oolitic calcareous rocks (named *Repedea Limestone*) specific to the area of Iasi city proximity, collected from the road bustling intersection "Podul de Piatră" (Stone Bridge) in Iasi [19,20]. These rocks were aged in natural conditions and a black crust was formed by gravimetric deposition of atmospheric particles. The elemental compositions were analyzed both on the black crust (outside) and on the part unaffected by pollution (inside) keeping the same experimental conditions. Fig. 2 displays an overview of the 200–350 nm spectral range (where was possible to see differences between the two zones), recorded with a Nd:Yag laser (Quantel Brilliant Eazy, 532 nm, 10 ns). The energy/pulse employed was 50 mJ, for an impact spot diameter of 1.4 mm leading to fluence of 3.2 J/cm^2. There are visible the spectral lines belonging to the limestone and crust. Because of atmosphere pollution influence, we must underline the presence of some compounds typical for Saharan dust (Si) but also metallic compounds typical for urban industrial aerosols (Fe, Mg). Therefore, preliminary LIBS measurements evidenced a strong difference in the intensity of some elements (example Fe I, II; Mg I, typical for metallic particles), their intensity being higher in the crust (Fig. 2). The optical emissions plasma plume seems to be very sensitive between the two studied cases. Moreover, the optical emission spectra appear to be very sensitive to the polluted area of the limestone sample.

The other investigation method used, SEM/EDX (Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy, Vega II LSH – Tescan, coupled Quantax QX2 – Bruker – Roentec) provided information about the morphology and elemental composition of limestone and crust. SEM images of the external and internal surfaces of the prelevated sample and the chemical elemental compositions determined from EDX spectra are presented in Fig. 3a–d.

SEM images and the elemental compositions of the outside and inside of the rock show the alteration of the surface morphology and chemical composition due to the deposition of atmospheric dust. The elemental composition analysis on oolitic rock provides important information regarding the impurities deposited in time. The chemical investigations evidenced elements such as Fe and Mg among others. These elements present as metallic nanoparticles could affect the thermal behavior of limestone substrate when pulsed laser irradiation applied, and this is why we will take into consideration in our simulation.

2.3. Work in COMSOL

The two materials, the deposited crust and the limestone rock, are non-homogeneous materials, where different elements and chemical substances are in contact. For that reason, the local behavior of the crust when irradiated with pulsed laser and the induced heating effects over the limestone support due to thermal diffusion by conduction are important to be studied. It is known that calcium carbonate, as a part of limestone composition, does not absorb laser irradiation [26], therefore, the thermal threshold is supposed to be due to heat diffusion from the other materials and elements. From all the elements evidenced by chemical analysis, metalic iron and metalic magnesium (Fe I and Mg I lines in Fig. 2) are the elements