

## Evaluation of Electron Density and Excitation Temperature of Atoms in a Concrete by Laser-Induced Breakdown Spectroscopy

コンクリートを対象としたレーザー誘起ブレイクダウン分光法における  
電子密度および原子励起温度評価

Shuzo Eto, Shota Kinoshita, Takashi Fujii and Masayoshi Y. Tanaka  
江藤修三<sup>A,C</sup>, 木下翔太<sup>B</sup>, 藤井隆<sup>A</sup>, 田中雅慶<sup>C</sup>

*CRIEPI<sup>A</sup>, Tokyo Tech<sup>B</sup>, IGSES Kyushu. Univ.<sup>C</sup>*  
2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan<sup>A</sup>  
電中研<sup>A</sup>, 東工大<sup>B</sup>, 九大総理工<sup>C</sup> 〒240-0196 横須賀市長坂2-6-1<sup>A</sup>

Laser-induced breakdown spectroscopy (LIBS) was performed to measure the chlorine concentration in a concrete. In order to enhance the chlorine emission intensity, two laser pulses were irradiated on the target. Electron density and excitation temperature of atom are evaluated by use of Stark broadening of hydrogen line and Boltzmann plot of iron emission intensities, and is found to decrease with the gate delay of Intensified CCD camera from laser irradiation. The results are consistent with the phenomena that the laser-induced plasma expands and dissipates in time, and are considered to be used for the qualitative description of the mechanism of the emission enhancement.

### 1. Introduction

Reinforced concrete (RC) is widely used for a large structure or building. When a RC structure is located on the sea side area, salt particles in air or sea water attach on a surface of the RC structure. The reinforcing bar in the concrete is eroded by chlorine in sea water due to the penetration from the surface of the RC structure.

Potentiometric titration (PT) is commonly used for the measurement of chlorine ions in concrete [1]. It takes a lot of time to crush and grind the concrete, which is necessary for chemical analysis in PT. On the other hand, Laser-induced breakdown spectroscopy (LIBS) can directly analyzed the elements in concrete by laser irradiation at the surface of a concrete [2-5]. In the present work, we performed the experiment of LIBS by use of two laser pulses and measured the emission intensity of elements including chlorine, and evaluated the electron density ( $N_e$ ) and excitation temperature of atoms ( $T_{ex}$ ) to reveal the mechanism of the emission intensity dependence on the experimental condition.

### 2. Experimental setup

The experimental setup is shown in Fig. 1. Nd:YAG laser pulses (532 nm, pulse width ~ 10 ns) are focused on the surface of the target. In the experiment, the configuration, in which laser 1 was only used for laser irradiation, was called as single-pulse (SP) configuration, and the configuration, in which laser 1 and 2 were used for laser irradiation, was called as double-pulse (DP)

configuration. The laser pulses of laser 1 and 2 were superposed to irradiate the target using the polarization beam splitter. Timing controller (Stanford Research Systems, DG645) was used for the synchronization of the Intensified CCD (ICCD) camera, the laser 1 and 2. The emission of laser-induced plasma was collected by use of lens and focused on the edge of the bundle fiber. The spectrometer (Roper Scientific, SpectraPro 2300i) and ICCD camera (Roper Scientific, PI-MAX 1k) were used for analyzing the emission spectra. The energies of laser 1 and 2 were set to 5 and 25 mJ, respectively, and the time interval between laser 1 and 2 was set to 0 s and 0.3  $\mu$ s for SP and DP configuration. The exposure time of ICCD camera was set to 0.2  $\mu$ s to measure the gate delay from laser irradiation ( $t_g$ ) dependence on spectral intensity.

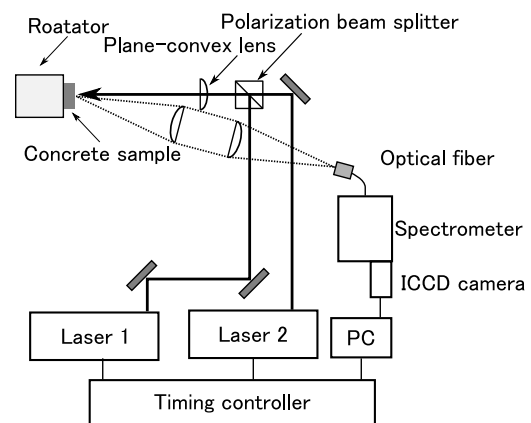


Fig. 1. Experimental setup of LIBS

The chlorine concentration in concrete was set by adding the sodium chloride into the fresh concrete, and measured by use of PT after crashing and grinding the concrete. The powder of the concrete was pressed into the frames with a 30 mm diameter by applying a pressure of 10 MPa, and used for the LIBS experiment.

### 3. Experimental results

The DP configuration contributed to the enhancement of chlorine emission intensity even when the energy was lower than 30 mJ [5, 6]. The result is attributed to the change of the population of atoms in each upper level. The population of atoms is affected by  $N_e$  and  $T_{ex}$ . These parameters were evaluated by the emission spectra analysis in the experiment.

#### 3.1 Evaluation of electron density

$N_e$  was evaluated from the Stark broadening of hydrogen line at the wavelength of 656.28 nm. Electron temperature of the laser-induced plasma was assumed as 1 eV to evaluate  $N_e$ . The  $N_e$  dependences on  $t_g$  are shown in Fig. 2. The quantity of  $N_e$  decrease with  $t_g$  monotonically in SP and DP configuration. The quantity of  $N_e$  in DP is slightly higher than that in SP in all ranges of  $t_g$ .

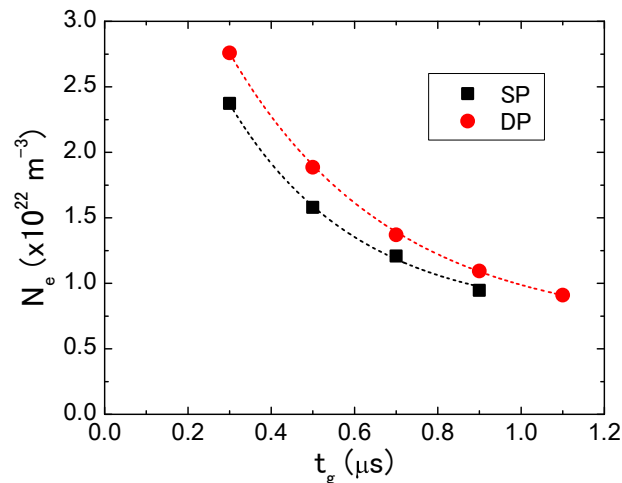


Fig. 2. Electron density dependence on gate delay from laser pulse irradiation

#### 3.2 Evaluation of excitation temperature of atom

$T_{ex}$  was evaluated from the Boltzmann plots of iron lines at the wavelength of 429.92, 487.821, 517.16 and 639.07 nm. In order to measure the iron emission lines simultaneously, the wavelength range from 400 to 670 nm was measured by use of a grating with 150 grooves/mm. Although the candidate lines of iron for Boltzmann plots were observed at the wavelength region, the emission

lines of iron except for the above 4 lines were not used for the Boltzmann plot owing to the spectrum interference with other emission lines. The temperature decreases monotonically with  $t_g$  in SP and DP configurations with the same trend.

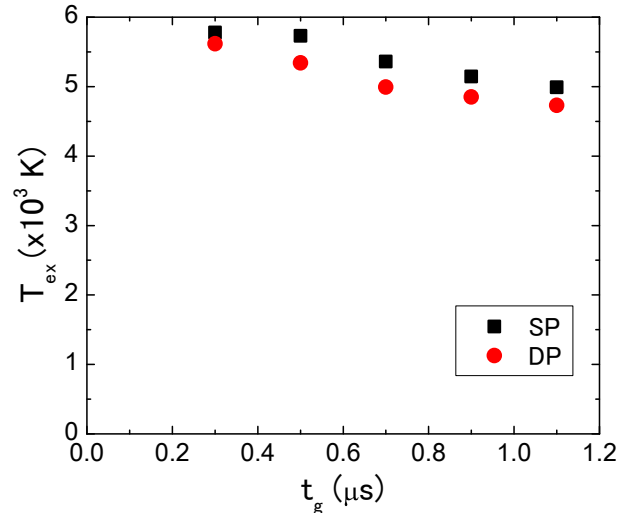


Fig. 3. Excitation temperature of atom dependence on gate delay from laser pulse irradiation

### 4. Conclusions

The quantities of  $N_e$  and  $T_{ex}$  were evaluated by Stark broadening of hydrogen emission line and Boltzmann plot of iron emission intensities in SP and DP LIBS for concrete. Although there were not large differences of  $N_e$  and  $T_{ex}$  between SP and DP configurations when the total energy was 30 mJ,  $N_e$  and  $T_{ex}$  dependences on  $t_g$  were observed. The decrease of  $N_e$  and  $T_{ex}$  is reasonable from the point of view that the laser-induced plasma expands and dissipates with  $t_g$ . The evaluation of  $N_e$  and  $T_{ex}$  shown in this study will contribute to reveal the mechanism of emission enhancement in DP configuration.

### References

- [1] JIS A 1154:2012. Methods of test for chloride ion content in hardened concrete.
- [2] G. Wilsch, F. Weritz, D. Schaurich and H. Wigenhauser: *Constr. Build. Mater.*, **19** (2005) 724-730.
- [3] F. Weritz, D. Schaurich, A. Taffe and G. Wilsch: *Anal. Bioanal. Chem.*, **385** (2006) 248-255.
- [4] K. Sugiyama, T. Fujii, T. Matsumura, Y. Shioyama, M. Yamaguchi and K. Nemoto: *Appl. Optics*, **49** (2010) C181-C190.
- [5] S. Eto, T. Matsuo, T. Matsumura, T. Fujii and M. Y. Masayoshi: *Spectrochim. Acta B*, **101** (2014) 245-253.
- [6] S. Eto, J. Tani, K. Shirai and T. Fujii, *Spectrochim. Acta B*, **87** (2013) 74-80.