Laser-induced breakdown spectroscopy for rapid detection of corrosiveness in concrete

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Abstract. Identification of corrosiveness in concrete is necessary for evaluation of building strength. In this study, identification of reinforced concrete corrosion has been successfully conducted using laser-induced breakdown spectroscopy (LIBS) method by identification of sodium element as a fingerprint in the sample. Low-power neodymium yttrium aluminum garnet (Nd:YAG) laser was used (1064 nm, 34mJ, 7ns) as an energy source. The laser beam was focused on concrete sample surface which contains different concentration of sodium-chloride (0.1 % - 1%). The experiment was carried out under atmospheric pressure. The sodium emission line at Na I 589.59 nm was successfully detected. Nice linear calibration curve of sodium line in concrete containing different concentration of sodium chloride (NaCl) was made. The linear curve certified that sodium line can be used as a fingerprint for evaluation of concrete strength.

1. Introduction
Reinforced concrete takes important rule as the basic component of modern infrastructure development, such as for construction of buildings, bridges, highways and so on [1,2]. Thus identification of concrete corrosion is very important because concrete corrosion can cause cracks in concrete that under certain conditions can cause the collapse of buildings and endanger human life. This also will impact on fund requirement for infrastructure repairmen [3].

In marine environment, the concrete age relatively decreases due to direct contact with high concentration of sodium-chloride in the sea water [4]. The corrosion caused by the penetration of sodium-chloride through the concrete cracks slowly reduced its strength. If this continues for a long time, the concrete will be eventually broken [5-7]. Considering the reasons, the detection of corrosion of concrete becomes an important concern.

There are some methods to detect the concrete corrosion, such as surface potential (SS) technique, embedded corrosion instrument (ECI) [8], optical fiber sensor [9], and Ultrasonic Tomography (UT) [10]. But those methods have disadvantages, naley, the tools have to be placed directly to concrete, so the installation and equipments are relatively complex. Some cannot use small amount and thin samples, and some of them are relatively expensive. Another simpler way to detect corrosion of...
Concrete is by identifying the content of elements that present in the concrete. The methods that can be used are X-ray fluorescence (XRF) [11] and inductively coupled plasma emission spectroscopy (ICP-ES) [12]. However, those methods are not really practical because they need complicated sample preparation, thus it takes more time to complete the analysis.

On the other hand, laser induced breakdown spectroscopy (LIBS) provides a solution to the shortcomings. LIBS is a method that using pulse laser to evaporate and excite a small mass of sample surface, it creates plasma that contains special emission for each component in sample [13, 14]. This method requires very simple even no sample preparation, can be use for any kind of material under any atmosphere pressure, and provides rapid material analysis [14,15]. It also can be use for any kind of material including metal [16] and non-metal [15, 17].

In this study, the identification of concrete corrosion using LIBS methods will be conducted. The concrete spectra containing sodium will be showed. The measurement of plasma stability and calibration curve will be carried out to show our equipment stability.

2. Method

In this study, a pulse Nd:YAG laser (New Wave Research, Polaris II 20 Hz) with 1064 nm in wavelength was used as an energy source. The laser beam was reflected to the silver mirror then focused by convex lens to the sample that located inside the camb. A luminous plasma was produced when the laser beam impinged the sample surface. The induced-plasma emission was detected by an optical multichannel analyzer (OMA) with the aid of optical fiber that connected OMA (LamdaVision SA-100W-HPCB1024/C type). The experimental set-up used in this study was shown in Fig. 1.

The laser beam energy, repetition rate and pulse width were 34 mJ, 10 Hz, and 7 ns, respectively. This study was conducted under atmospheric pressure. The samples used in this study were concrete cement with addition of sodium-chloride. There are eight samples used in this study, each sample contains different concentration of sodium from natrium-chloride (NaCl) of 0.1%, 0.25%, 0.5 %, 0.75%, 1 %.

3. Results and discussion

In this experiment, a laser pulse with a narrow pulse width (7 ns) was used. The laser peak power is very high. The laser beam was focused by a convex lens which increases the peak power of the laser beam. When the laser beam hits the sample surface, a small amount of the sample will evaporate. Due to high peak power of laser, the evaporated sample then undergoes atomization into its constituent
materials due to high energy, and finally the sample also undergoes ionization and excitation. As the nature of the atom, after the ionization process, the atoms are undergo de-excitation by releasing their energy in the form of electromagnetic waves radiation at a certain wavelength. The resulting emitting light is called laser plasma. The color of the produced plasma that was produced depends on the type of the constituent elements. The emission of the plasma was then detected by OMA system, and the intensity and wavelength of the sample elements were obtained. The wavelength of each peak (the element with relatively high intensity) obtained ware then matched with the NIST standard reference data to determine the name of the elements.

Figures 2(a) shows the emission spectrum of concrete sample with (red line) and without (blue) addition of NaCl. From that spectrum, we can clearly see the spectrum lines of Ca and Na in the case of concrete containing sodium (red line). However, it should be noticed that completely no Na line (Na I 589.59 nm) appears in the concrete without sodium line. Calcium was emitted from the concrete material, which contains Ca as major element. The higher peak is ionic Ca lines at wavelengths of 393.37 nm and 396.85 nm, while the neutral sodium line is at 589.59 nm wavelength. The result confirmed that the present method can be employed to detection of Na in concrete for evaluation of concrete from the corrosiveness.

Figure 2(b) shows the emission spectrum obtained from the concrete sample with addition of sodium at certain concentration. The red line shows the concrete sample with the highest sodium intensity (1% sodium), while the blue line shows concrete spectrum with the lowest sodium intensity (0.1% sodium). It was confirmed that the higher concentration of sodium, the higher emission intensity of sodium as displayed in Fig. 2(b).

On the other hand, sodium is one of the causes of the corrosiveness in concrete, and it can be seen using LIBS. Therefore, LIBS can be used to detect the corrosiveness in concrete. Those spectra above also show that LIBS can detect atomic and ionic line of the components. Besides, we conducted the measurement of plasma stability by calculating the ratio intensity of Na and Ca for several shots. Ratio intensities of Ca and Na for several shots are 0.332, 0.332, 0.337, 0.353 and 0.336, respectively. The plasma stability curve is shown in figure 3 (a).
This indicates that LIBS can capture the intensity in several number of shots with relatively the same ratio intensity of Ca and Na, which confirm that the plasma has good stability and it has a potential for quantitative analysis. Thus, it has high possibility to conduct quantitative analysis of concrete corrosion in concrete by means of sodium detection in concrete. A typical calibration curve for concrete sample containing various concentrations of sodium is shown in figure 3(b). The curve shows the relation between sodium concentration and intensity of sodium detected at 589.59 nm. The intensity of sodium detected and concentration of sodium in sample shows a linear characteristic, with least square fit $R^2 = 0.9984$.

4. Conclusion
Corrosion detection by identifying sodium content in concrete using LIBS methods has been successfully performed. LIBS methods can be used for analysis with simple or even no sample preparation, requires relatively cheap equipment, and provides rapid sample analysis. By using the LIBS method, the calcium and sodium spectrum lines in concrete can be clearly identified. Concrete sample with 1% sodium content shows the highest sodium intensity, while concrete sample of 0.1 sodium addition shows lowest sodium intensity. To see the methods stability, we carried out the calculation of plasma stability curve. It shows that LIBS can detect plasma with relatively same intensity, therefore the plasma emission is quite stable, so it might be possible to use to detect the corrosiveness of reinforced concrete.

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