Analysis of calcium element in concrete using laser-induced breakdown spectroscopy

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Abstract. One of the spectroscopy method, which can determine constituent in material, is Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is an atomic emission method that uses radiation pulses from the high energy laser. LIBS allows the detection of spectral lines of elements present in the excited sample. In this present research, a pulse Nd: YAG laser with 1064 nm wavelength was used in LIBS system to the analysis of concrete elements. Spectrum analysis of calcium element in concrete was performed to understand the characteristics of generated laser plasma. Characteristics of laser plasma were shown through energy and pulse repetition rate laser variations. Using the higher energy laser, the larger plasma diameter was made. Furthermore, the graphs show increment in intensity and peaks, which have better sharpness. The laser repetition rate does not affect the size of the plasma, but the greater frequency of laser shots cause the lower emission intensity.

1. Introduction
There are several methods of calcium concentration analysis such as Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Atomic Absorption Spectrometry (AAS) which have high sensitivity, but it is very expensive, complex, time-consuming and laborious preparation sample [1,2]. X-ray fluorescence spectrometry can also be used as an analysis calcium concentration method, but it is harmful to the human body [3].

One of the spectrochemical method, which can determine constituent in material, is Laser-Induced Breakdown Spectroscopy (LIBS) [4]. LIBS is an atomic emission method that uses radiation pulses from high energy laser. LIBS allows the detection of spectral lines of elements present in the excited sample. One of the advantages of technical LIBS is the capability to analyze the substances in any states, as well as solid, liquid or gaseous, even in colloids as aerosols, gels, and others [5].

Analysis of material in concrete is performed using calcium element because it is the highest element concentration in concrete [6,7]. In this study, optimization of laser plasma with laser energy and pulse repetition rate will be conducted. Photograph and spectrum of concrete containing various kind of calcium wavelength will be carried out to show the characteristics of plasma laser.

2. Method
Concrete is used as the object of research in this time because the concrete contains a calcium element with a high concentration of about 50% [8]. Laser plasma spectroscopy method was performed on concrete samples with two variations of laser energy and pulse repetition rate. The laser energy used is...
PFN of 85% and 90%. While the frequency of laser shots is 10 Hz and 15 Hz. The environmental pressure is adjusted to a pressure of 400 Pa.

Figure 1 is a tool scheme which prepared to test the elemental content using laser spectroscopy method. The laser is shooting Nd: YAG 1064 nm (2) is configured using software integrated into the computer (1). The laser beam is directed to hit sample inside the chamber (5) using a silver mirror (3). The lens (4) with a focal point of 10 cm is placed in front of the chamber to focus the laser so that the beam of the sample is sharp. The pump (6) is also provided for lowering pressure in the chamber. After the laser hit the sample, laser plasma will be formed that carries the optical information in the sample.

Light from the plasma then captured by optic fiber (7) and subsequently brought to Optical Multichannel Analyzer (OMA) (8). OMA and "Spectra Lab 2.0" software analyze optical information and generate spectrum graphics that appear on the computer. The resulting graph is subsequently converted into Excel form to facilitate analysis of the elemental content spectrum present in the sample.

3. Results and Discussion
To produce the optimal Ca spectrum using laser spectroscopy method; several variables will be tested, including the effects of laser energy and pulse repetition rate.

3.1. Laser Energy Effect
This research uses a laser with maximum output energy of 50 mJ. Variations of energy tested were two using PFN of 85% (42.5 mJ) and 90% (45 mJ). The amount of laser energy given to the target is shown in the value of PFN (Pulse Forming Network) which is the percentage of the energy released to the total energy that laser can be produced [9].
Figure 2. Plasma photo taken from a concrete sample with laser energy variation (a) PFN 85% (b) PFN 90%

Figure 2 shows a plasma photo formed after the sample shot by a laser. Obtained results of plasma size at 85% PFN is 9 mm while at 90% PFN plasma produced with a size of 13 mm. Visually, it is apparent in Figure 2 that the 85% PFN forms a plasma with a smaller size compared to 90% PFN. Hussain and Gondal in their research also have tested the plasma size and obtained similar results that the greater the energy given, the larger the plasma size is formed. Increasing the laser pulse energy will increase the number of atoms that are stretched from the target surface and increase the thermal energy that changes to the fast kinetic energy of ions and electrons [10]. Furthermore, the ions and electrons in the plasma have a high speed and can propagate out of the target surface [11].

Figure 3. Concrete spectrum graphic with laser energy variation

Figure 3 presented an intensity graph concerning the wavelength of the concrete sample. It can be observed that the intensity generated at the overall wavelength (range 300 nm s.d. 500 nm) by 90% PFN is greater than 85% PFN. Spectra formed at 90% PFN such as at Ca II wavelength 318.1 nm, Ca II 373.7 nm, Ca II 393.4 nm, Ca I 422.7 nm, and Ca I 445.6 nm can be identified easily because it has good sharpness. In the spectrum produced by PFN of 85%, some spectra can be identified because the peak still looks sharp, as in Ca II 373.7 nm, Ca II 393.4 nm, and Ca I 445.6 nm. However, at the wavelength of Ca II 318.1 nm and Ca I 422.7 nm, the peaks are visible sloping so that the identification of the spectrum becomes more difficult. Spectrum intensity ratio and 90% PFN background and 85% PFN in Figure 3 respectively were 7.37 and 6.37. The intensity ratio indicates that an increase in laser energy will improve the quality of the spectrum formed.

The interaction between the nanosecond pulsed laser and the dominated material is predominantly characterized by explosive smelting and evaporation from the target surface resulting in microscopic
flow from the hot melt point to the firing path. The intensity of the spectrum increases with the increase of laser energy due to the increase in the amount of the material [12].

3.2. Pulse Repetition Rate Effect

Variation of laser pulse repetition rate is also carried out on this research. The repetition rate is the number of fired laser emissions every single second. Shooting frequency variations are used is 10 Hz and 15 Hz, while the pressure and energy parameters are the same at 400 Pa and 90% PFN.

Figure 4. Plasma photograph taken from a concrete sample with pulse repetition rate variation (a) 10 Hz (b) 15 Hz

Figure 4 shows the plasma form of the pulse repetition rate variations which tested on the concrete sample. The colors formed from both experiments emit orange light. The diameter of plasma at 10 Hz and 15 Hz are the same sizes, which is 13 mm. Both of them has two plasma regions, namely primary plasma and secondary plasma. The same size indicates that laser interaction to samples using both 10 Hz and 15 Hz shooting frequencies produces a crater that is not much different [13].

The plasma formed next captured by OMA and produced a spectrum graph as shown in Figure 5. The contrast can be seen in the intensity that is formed. The pulse repetition rate of 15 Hz produces a lower intensity compared to the 10 Hz shooting frequency. At the frequency of 15 Hz shot is found that the peak 396.8 nm Ca II has an intensity of 1140. While the treatment by using the frequency of 10 Hz shot obtained peak intensity of 1577. Spectrum and background intensity ratio formed from the frequency of 10 Hz and 15 Hz shot successively are 11.1157 and 8.1145. The intensity ratio of 10 Hz is greater than 15 Hz. This suggests that improving the quality of the spectrum can be achieved by decreasing the frequency of laser shots.

In the plasma laser spectroscopy method, the increment of pulse repetition rate decreases the intensity of the wavelength. At high frequencies, particles will accumulate in front of the surface and plasma generation is performed both from the gas formation and from the sample surface. The released particle from the sample accumulated in front of the laser cause energy transmitted to the sample is reduced. The release of particles produces plasma generation above the sample, absorption, and laser radiation scattering on the particles. The number of particles will increase with increasing laser pulse repetition rate [14]. The buildup causes ablation caused by laser explosions that are absorbed/diffused by the impurities [13]. Absorption that causes laser radiation unable to achieve a target called the plasma shielding effect [15].
4. Conclusion
There are two kinds of variations to determine the characteristics of the laser plasma that is formed: namely laser energy and pulse repetition rate. The higher the laser energy used, the larger plasma diameter produced. The spectrum graphs also have increased in intensity and peaks that have better sharpness. Variations in the frequency of laser shots do not affect the size of the plasma, but the greater the frequency of laser shots used causes to lower the intensity of the spectrum.

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