Detection of sulfur in the reinforced concrete structures using a dual pulsed LIBS system

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ABSTRACT

In concrete structures, an excessive amount of sulfate ions can cause severe damage to the strength and the stability of the building structures and hence a sensitive and reliable technique for sulfate ion detection in concrete is highly desirable. Laser-induced breakdown spectroscopy (LIBS) is one of the most reliable and sensitive techniques to identify the presence of potentially dangerous sulfur in the concrete structure. The atomic emission lines of sulfur lying in the 200–900 nm region are mostly singly ionized states and hence inherently very weak. In order to enhance the sensitivity of the conventional LIBS system, we employed a dual pulsed LIBS system for detection of weak spectral line of sulfur in concrete using the S II peak at 545.38 nm as a marker for quantifying sulfur content in the concrete. The 1064 nm fundamental and 266 nm fourth harmonic of the Nd:YAG laser in conjunction with Spectrograph/gated ICCD camera are the core factors in improvement of sensitivity. Furthermore, the dual pulsed LIBS system and the fine maneuvering of the gate parameters and interpulse delay yielded improvement in the sensitivity, and resulted in a systematic correlation of the LIBS signal with the concentration of sulfur in the concrete sample. In order to quantify the sulfur content in concrete, a calibration curve was also drawn by recording the LIBS spectra of sample having sulfur in various concentrations. The limit of detection achieved with our dual pulsed LIBS system is approximately 38 μg/g.

1. Introduction

Sulfur has been proposed to be added to concrete materials as a cementing agent in early 1900 [1]. There are many examples of sulfur uses in concrete and a patent was allotted in 1900 for sulfur uses in roofing, pavement, coating and jointing or grouting compounds for strengthening of structures [2,3]. Earlier it was reported that sulfur mixed concrete has no shrinkage as it has different thermal coefficient of sulfur than steel and sulfur mixed concrete behaves like epoxy compounds [2,3]. Recent study demonstrated that the presence of excessive amount of sulfate ions causes great deal of damage to the strength and stability of the concrete structures. When sulfate ions react with the hydrated calcium aluminate or the calcium hydroxide components of hardened cement, calcium sulfoaluminate hydrate known as ettringite is developed [4–6]. These new crystals cause the concrete to crack and spall, which is technically known as sulfate attack in concrete. These chemical reactions between

sulfates and the cementitious material lead to destruction of the concrete structure and decrease in the strength of the overall structure. Due to these reasons, the sulfate content determination in concrete is essential for damage assessment before reconstruction and even during the repair works. According to British Standards, BS 5328 1997, the allowable limit of sulfate concentration in concrete is 0.60% by weight of concrete (or 4.0% by weight of cement) [7].

There are many chemical and analytical techniques like induction coupled plasma-atomic emission spectroscopy (ICP-AES), XRF and other analytical methods for elemental analysis requiring very cumbersome sample preparation, preservation and transportation. Besides inherent difficulties in these analytical methods, the methods are slow, less selective, less sensitive and destructive in nature [8]. In a typical wet chemical method, the concrete samples are obtained from the structure, transported to the laboratory, where they are cut into small pieces, ground and dissolved in hydrochloric acid. The content of the acid soluble sulfates is determined gravimetrically from the precipitation as $BaSO_4$ [9]. In ICP-AES, the sample is introduced as a droplet into argon plasma at about 10,000 °C in this case also the sample preparation is a quite lengthy process. Considering high directionality of the laser,

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it could be a natural tool for the analysis of the concrete structure. There are many laser based emission and excitation spectroscopic techniques but the selectivity of these methods is not appreciable enough to deal with a complex system like concrete. Laser-induced breakdown spectroscopy (LIBS) has been used as a powerful analytical technique for elemental analysis since it was introduced. A high power laser beam is focused on the material to be analyzed and the plasma generated is analyzed using a proper gated spectroscopic system. The hot plasma of the elements cools down after certain time in the order of microseconds (or even in nanoseconds) and afterwards the atomic transitions take by emitting the characteristic atomic transition lines. In the case of LIBS, the emission from the neutral singly ionized and doubly ionized species is characterized. From the mechanism of LIBS, it has many positive attributes like being highly selective, sensitive, non-destructive, rapid and direct sampling methods of analysis. Besides, LIBS can be used for remote analysis of the sample [10–13] and can be used in a harsh environment. LIBS system has been used for numerous applications [8,14–21] Although LIBS can very well be applied for the elemental analysis of concrete samples, the potentially hazardous elements like sulfur need further improvement of the conventional LIBS system.

In an improved version of LIBS, two laser pulses hitting the sample with a user-chosen interpulse delay are employed and these will have a considerable level of signal enhancement. Although signal enhancement in the dual pulsed LIBS system is consistently observed by almost all the research groups, the mechanism behind it is not so clear yet. There have been many explanations given in terms of interpulse delay time, increased pulse–plasma coupling, increased sample heating, and ambient gas rarefaction [22]. Forsman et al. [23] observed a higher mass removal rate when the interpulse delay time was increased in the range of 30–150 ns, and this was explained by a mechanism of ablation of the target by heated ejecta, which is produced by the first laser pulse, and subsequently heated by the second laser pulse. In general, it is believed that the reduction of ambient gas density is a result of the first laser pulse, which yields a faster vapor plume expansion and less effective shielding of the second laser pulse [24–26]. St-Onge et al. [27] studied the enhanced LIBS signals with the dual pulse combination of 1064 nm and 266 nm laser pulses and observed the larger signal enhancements for ionic lines than for atomic lines, which were also correlated with a higher plume temperature. Also they reported that optimum interpulse delay time is around 100 ns for atomic lines and about 3 μs for ionic lines. The plasma irreproducibility in conventional LIBS is caused by laser instabilities, ablation irreproducibility and sample non-homogeneity, all resulting in a relative standard deviation on the order of 5–10% [23,28]. LIBS sensitivity is improved due to a better coupling of the laser energy to the target and ablated material. Different versions of double pulsed LIBS system, in terms of the laser geometry and excitation wavelength, have been tried: splitting a single beam of same wavelength into two beams, two different wavelengths from two lasers and laser beam exciting the sample collinearly or orthogonally are different modes of dual pulsed LIBS operation [26,29–32].

Detecting sulfur in the multielemental sample like concrete is really challenging due to many reasons: first of all the strong emission lines of neutral sulfur are in vacuum UV and near IR regions and only weak lines from singly ionized sulfur are present in the 200–900 nm regions. Secondly sulfur is highly reactive in the excited state and quickly reacts with oxygen. Moreover, in the case of the multielemental sample like concrete the emission is reabsorbed by other elements and for these reasons the works regarding the detection of sulfur using LIBS are so limited [33]. The first attempt to detect sulfur was done by Salle et al. [34]; in

their work to detect elements in the stimulated Martian atmosphere (in the presence of CO_2) they used relatively weak atomic transition lines of S II at 543.28 and 545.38 nm as marker and curiously these two lines are found to be so strong only in the stimulated Martian atmosphere and in the normal condition these transition lines are rather feeble. LIBS system has been also employed to detect sulfur in the concrete samples. Gaft et al. [35] used four three- harmonics of Nd:YAG laser as an excitation source in both single pulsed and dual pulsed LIBS to determine sulfur in minerals under ambient condition and detected sulfur contents in the green visible region (544.99 nm) for sulfur bearing minerals. Recently Assimellis et al. [36] proposed another marker wavelength around 868 nm for the detection of sulfur using LIBS. Jasik et al. [37] and Radivojevic et al. [38,39] used a strong VUV atomic transition line of sulfur at 180 nm to detect sulfur in polymer. In a recent elaborate paper, Dyar's group [40,41] used few peaks around 543.28 nm of sulfur to carry out the statistical analysis of detecting sulfur in the geological sample.

In the case of detection of sulfur in concrete sample, a design of a portable system has been put forward by Taffe et al. [42]; when it comes to detection of sulfur in concrete sample, the works of Weritz et al. [43–45] stand out. Weritz et al. used a single pulsed LIBS system with S I atomic transition lines at 921.3 nm as marker. The 921.3 nm transition line is in the near infrared region and it is at the close proximity of the oxygen line at 926.6 nm. In their work the data for 0.6% by weight is the minimum detection limit. Although 921.3 nm atomic transition line is one of the strongest lines of S I, the limit of detection is not that appreciable. In the case of sulfur, there are quite a few strong transition lines of S I below 200 nm. As mentioned before, the sulfur atom is highly reactive at the excited state and can easily react with the available oxygen and as the concrete sample has oxygen, using the VUV wavelengths as a marker is not reliable. S I also has many atomic transition lines in the near IR region, one of these lines (921.3 nm) was used by Weritz et al. as a marker. In the case of concrete sample it is abundant with the calcium element and the singly ionized calcium atom (Ca II) has a strong atomic transition line exactly at 921.3 nm [46], which coincides with 921.3 mm marker and also it is possible that this 921.3 nm emission line is self absorbed by the sample itself, resulting in a weak LIBS signal. Also at the neighborhood of 921.3 nm, the atomic transition line of oxygen is at 926.6 nm and this oxygen line cannot be used as a reference line to study the relative growth of 921.3 nm marker line, because in addition to the sample, oxygen is present in the environment that will alter the strength of 926.6 nm line of oxygen.

In this work we developed a dual pulsed LIBS system for the detection of sulfur in the concrete sample [47], and doing so, we were able to improve the signal strength and make use of other general merits of the dual pulsed system described above. The two lasers radiations used in this work are 1064 nm and 266 nm from two different lasers and an emission line of S II at 545. 38 nm is used as a marker wavelength. We chose this transition line of S II in the visible region in spite of the fact that the line intensity is much smaller than its counterparts in the VUV and NIR regions due to the following reasons: the problem with the transition lines in the VUV region is sulfur is highly reactive and the signal level of sulfur is not that appreciable. In the NIR region, the calcium, which is a predominant element present in the concrete sample, has strong emission lines. Also in the 545.38 nm region, there is no overlap of the atomic lines of elements present in the concrete sample. Aluminum is one of the major elements present in the concrete sample, whose concentration remains constant and hence the transition line of Al II at 559.33 nm can be used as reference peak to study the variation of sulfur atomic transition peak. With the right choice of interpulse delay, detection gate delay