Online Sensor System Based on Laser-induced Breakdown Spectroscopy in Quality Inspection of Demolition Concrete

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Abstract
In the C2CA project, an online sensor system is required to measure and control the quality and homogeneity of demolition concrete continuously. Laser-induced breakdown spectroscopy is a candidate to fulfil the objective in several tasks. Investigated is the ability of LIBS as an online semi-quantitative composition analysis technique. The maximum laser repetition rate of 100 Hz and each measurement by single laser shot within 5 ms enable the online application in real time. The wavelength range between 273 nm and 326 nm is chosen for differentiations between mineral alloys and CaO powder. Principal component analysis is applied to differentiate between slag concrete, cement and calcium oxide samples, as based on the Ca II photon counts at 315.76 nm, 317.916 nm, 393.189 nm and 396.608 nm. The effects of different sample preparation procedures on the laser shot-to-shot repeatability are also characterized. The encouraging results indicate the eligibility of LIBS for online quality inspection of concrete products.

1.0 Introduction

Concrete is one of the most widely used artificial building materials. In the traditional routine concrete is produced using primary resources (e.g. aggregates and limestone for cement), while the end-of-life concrete is mixed with other recyclables to end up in low-grade constructions such as road foundations. Full recycling of the demolition concrete is a way to reduce the environmental impacts of the traditional routine, such as depletion of natural resources, consumption of energy and CO_2 emission. In a currently running European project [1], two buildings with 50.000 tons concrete waste are to be recycled to a clean calcium-silicate-rich fraction, serving as feedstock for cement production, and a clean silicate fraction, serving as aggregates, for reuse in new concrete. Specifically, the project investigates the possibilities to process and reuse the aggregates onsite to save on transport energy and further reduce the CO_2 footprint. In this way the building and demolition lifecycle may be closed for concrete. An online sensor system is required to measure and control the quality and homogeneity of the recyclables continuously. To that end the sensor system should fulfil different tasks. First, the contaminants in municipal buildings, such as wood, foam, gypsum, polymer, metals, glass, organic matter, must be detected in the waste flow. This may be achieved using a semi-quantitative method, able only to differentiate between different materials. Second, to control a processing unit, such as a mill or other machinery, the quality in terms of compositional variations of both the input material and output products needs to be monitored. This may also be achieved with a semi-quantitative method, but which will have to be able to detect a wider range of contaminants. Third, specific and determining contaminants such as high silicon content in cement, chlorine or sulphur, must be measured using a quantitative method. To facilitate all three tasks demands a rapid and versatile sensor system.

LIBS is an emerging method for rapid composition analysis in which a laser pulse is focused on the sample surface to generate a plasma. To that effect, the laser power density must exceed the breakdown threshold of the sample material, which is in the range 10^7-10^9 W/cm^2 [2, 3]. During the development of the plasma the specific atomic or ionic light emission gives information about the element composition of the sample material [4]. The emitted photon wavelength corresponds to the energy of the electron transition between two atomic or ionic energy levels and the photon count is proportional to the concentration of the element species in the sample [5]. As LIBS is a surface scanning method it is especially sensitive to the possible contaminations of concrete, as these contaminations always stick and/or diffuse inwards from the surface. By nature, LIBS facilitates stand-off capability and speed of measurement, both of which are essential for an online technique. It has already been around since the early 1990's, for example for detection of sulphur and chlorine in concrete [6-10] and major and minor elements in concrete [2, 10-12] and cement [13].

Several semi-quantitative applications of LIBS have been investigated, such as grouping techniques or pattern recognition using different emission intensities [14] and Rankin diagrams [15, 16]. The photon count ratio of the calcium (892.7 nm) and oxygen (926.6 nm) has been used to differentiate between aggregate and cement [10], while principal component analysis (PCA) is used to group and identify different classes of spectra [17-19].

The objective of this study is to use LIBS to differentiate between materials (Fe, Al, Cu, Ni, Pb alloys and CaO powder) with different major elements. When showing differentiability, this approach will be a candidate for the semi-quantitative technique required for contaminants inspection. By combining LIBS and PCA a differentiation may be made between different materials with the same major elements (slag concrete and cement), while allowing for a broad range of elements to be involved. This approach is a candidate for the semi-quantitative technique required for in-output control. The effects of different sample preparation methods on the laser shot-to-shot repeatability are characterized.

2.0 Methods and materials

A schematic for the experimental LIBS setup for concrete samples is shown in Fig. 1. The laser system is a diode pumped Q-switched Nd:YAG (Centurion, Quantel) operating at 1064 nm, pulse width 6.9 ns, pulse energy, 25.7 mJ and a maximum repetition rate of 100 shots per second The laser beam is focused by a convex lens of 200 mm focal length on the surface of the sample to generate the plasma. The diameter of the focused laser spot is ~300 μm and the laser power density is in the order of 1 GW/cm^2.
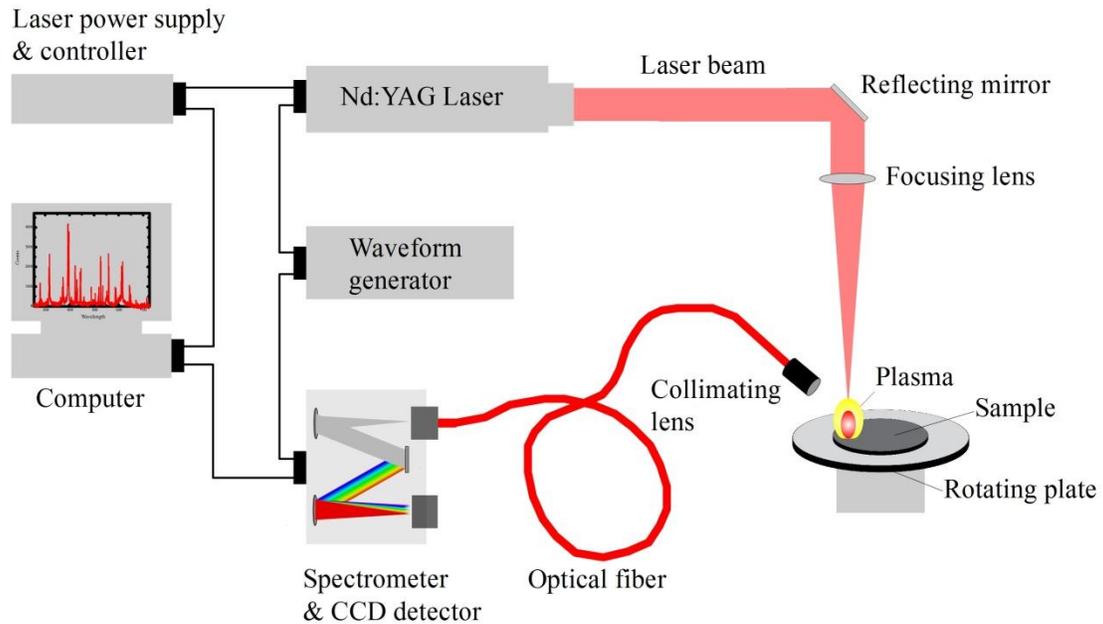
Fig. 1. Schematic of the LIBS experimental setup.

The light emission from the plasma is collected by a collimating lens (lens-to-sample distance 55 mm and collection angle 30°) and transmitted through a 2 m long silica optical fiber with numerical aperture 0.22. The receiving end of the fiber is coupled to a Czerny-Turner spectrometer (AvaSpec-3648) with a slit size 10 μm and a focal length 75 mm, operating in the pre-scan mode. The spectrometer is equipped with a 600 lines/mm grating, blazed at 400 nm and resolution 0.32 nm (FWHM). The spectrometer output is read by a built-in 3648 pixel CCD linear detector array (TOSHIBA 3648) within the bandwidth 250 nm to 770 nm. The laser and spectrometer are synchronized using a double output arbitrary waveform generator (Agilent 33521A, 30 MHz) with adjustable time delays and gate widths.

In this work a delay time of 12 μs and gate width of 10 μs are selected to collect the ionic and atomic photons from the cooling elements and to avoid the intense background initially created by the high-temperature plasma. Each measurement is related to a single laser shot. The spectrum captured by the CCD camera is transferred to the computer through a USB 2.0 cable. The spectrum of each measurement is read within a time frame of 5 ms, giving potentially a 100 Hz reading capability for several hundreds of spectra in view of the limited on-board memory capacity of the spectrograph. The sample is placed on a motorized rotating plate, moving with a constant velocity of 3 m/s. This simulates the movement of the concrete waste and the sampling of the waste as it would occur in practice.

2.1 Materials

The slag concrete sample is preprocessed by milling and sieving (1-2 mm). The slag concrete particles are then grinded and mixed with a wax binder (FLUXANA, Germany). Finally, the mixture is pressed into a pellet sample of 30 mm diameter and 2 mm thick using a pellet press. Using the same method but without the binder, cement types *I*, *III*/A and *III*/B powders are also pressed into pellets. Calcium oxide powder is directly pressed by hand. As a reference Mg, Fe, Al, Ni, Pb containing alloys are used.

3.0 Results and discussion

In order to carry out the multi-elemental analysis using LIBS without the loss of resolution, characteristic emission lines from different elements should be present simultaneously in a narrow bandwidth without significant overlap. The delay time and gate width are appropriately chosen as to avoid strong continuum background and spectral peak distortions due to self-absorption. The acquired LIBS spectra of the Mg, Fe, Al, Cu, Ni, Pb alloys and CaO powder are shown in Fig. 2 in the spectral range 273 nm to 326 nm. Each spectrum is the average of 12 laser pulses. The emission lines above three times the mean background level and without significant overlap are identified, referring to the online LIBS database from the US National Institute of Standards and Technology [20]. It proves that by detecting the major elements in different materials the differentiation between them can be easily made.
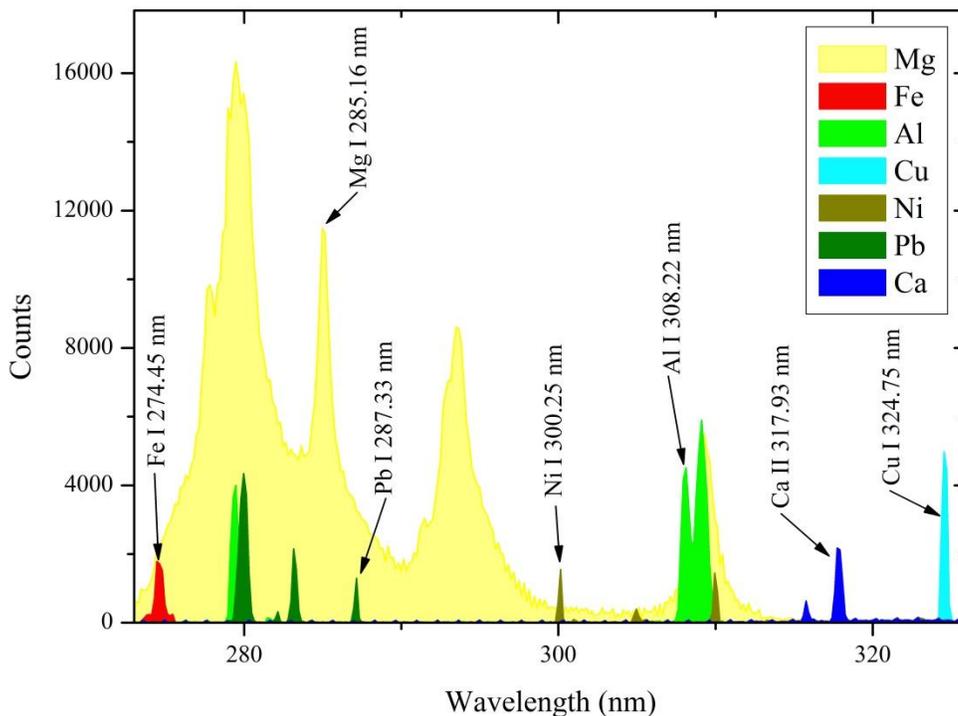
Fig. 2. Typical LIBS spectra for atomic (I) and ionic (II) lines between 273 and 326 nm after averaging 12 laser pulses..

In the 273-326 nm range each element contributed at least one emission line. One of the major challenges in LIBS spectral interpretation is that the spectrum is dominated by the major elements (high concentration), overlapping and obscuring the emission lines from minor elements (low concentration). To improve detection of the minor elements, the choices of bandwidth, delay time, gate width and method of compensation for the background noise prove crucial.

Fig. 3 shows the LIBS spectra in the range 385 nm to 480 nm of the slag concrete, Portland cement types *I*, *III*/A, *III*/B and CaO samples. The inset shows the spectral range 310 nm to 325 nm. Each spectrum is again the average of 12 laser pluses. Only four Ca *II* emission lines are observed (315.76 nm, 317.916 nm, 393.189 nm and 396.608 nm). The absence of the minor elements emissions may be attributed to the method of background noise compensation that was used here. It proves that LIBS is quite capable of detecting different materials. Next, it is investigated if the major elements in different sample materials show quite similar spectra or if LIBS is still capable of clearly differentiating between them. PCA is chosen as a suitable statistical method to this problem.
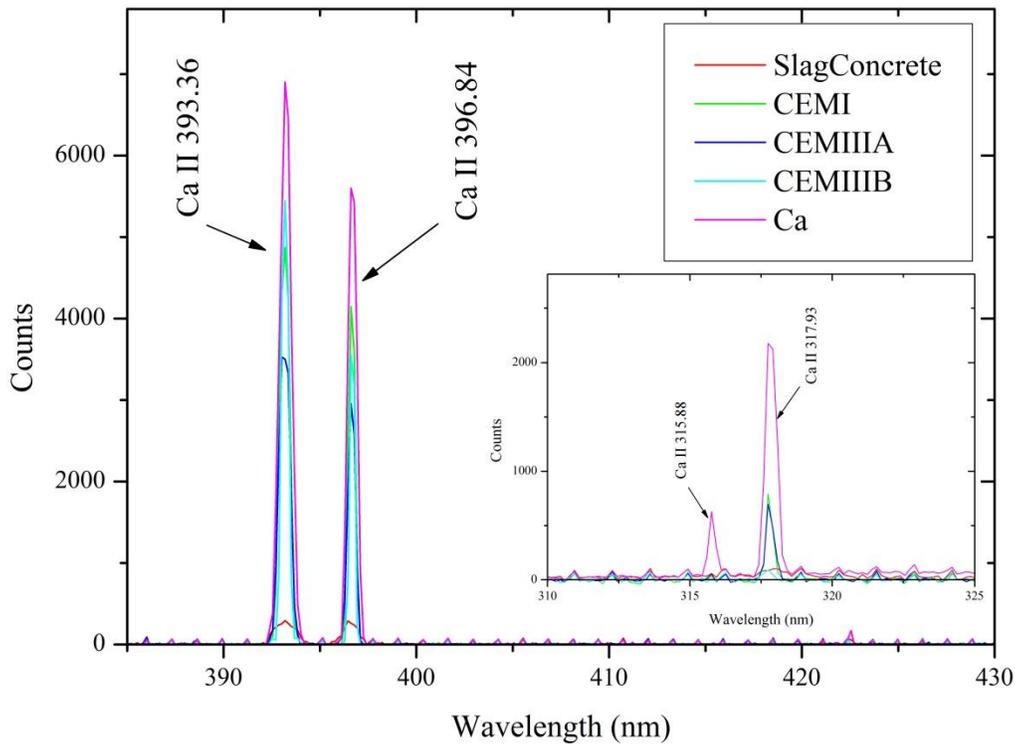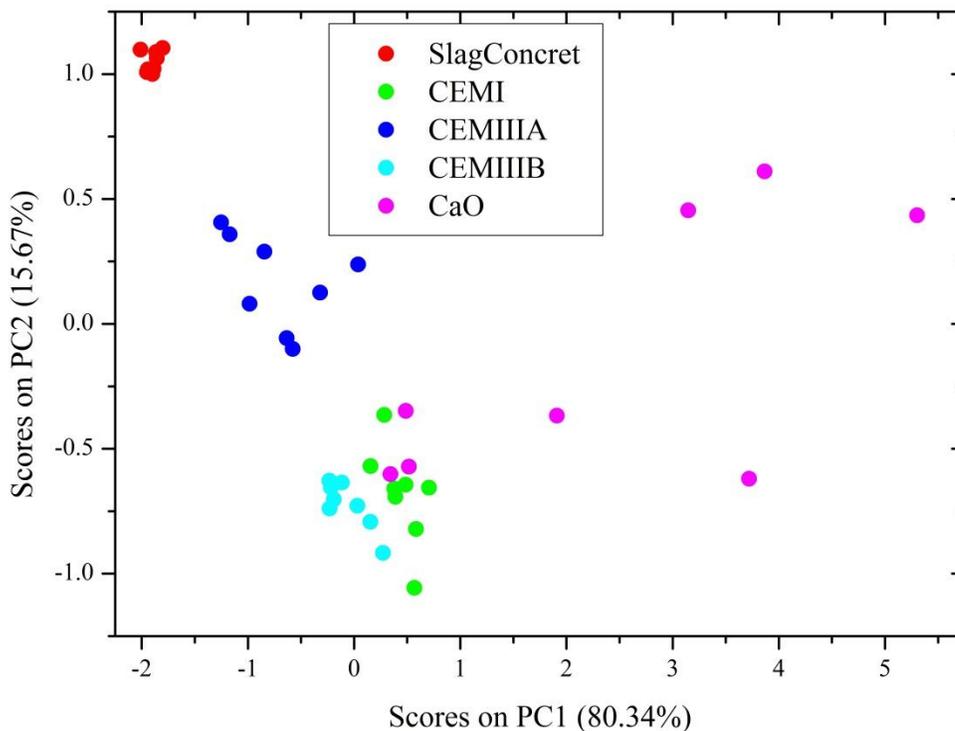
Fig. 3. LIBS spectra of slag concrete, Portland cement types *I*, *III*/A, *III*/B and calcium oxide samples between 385 and 430 nm. Inset: spectra between 310 and 325 nm.

PCA is a method where the spectrum, consisting of many wavelengths, is mathematically reduced to a limited number of values called principal components. Specially, the first principal component represents the most significant variations in the spectrum [21]. Using only the first two principal components the complicated spectrum is represented by a single point scattered in a two-dimensional plot (score plot), more or less precisely gathering the spectral points that belong to the same class. To guarantee representative results, a widely adopted criterion for PCA is that the minimum cumulative percentage to which principal components (PCs) contribute to the total variation should lie between 80% and 90% [22]. This may easily be achieved by adding more PCs. However, there is a drawback if the PCA involves too many wavelengths or a lot of noise. In that case many PCs may be required to meet the criterion, but also many of them may be useless in the identification.

        Prior to applying PCA the spectrum needs to be pre-processed to already condense the useful information and/or to suppress noise. To this effect the minimum gate width of 10 μs is used. The intensities of the Ca *II* emission lines (315.76 nm, 317.916 nm, 393.189 nm and 396.608 nm) are used as variables in the PCA method. Fig. 4 shows the score plot of the LIBS spectra collected for slag concrete, the Portland cement types *I*, *III*/A, *III*/B and for the CaO samples. The first two PCs account for 80.34% and 15.67% of the total variation, respectively. Hence, a two-dimensional score plot representing over 96% of the variation gives already a good approximation and, apparently, no more PCs

need to be included. Both the slag concrete and Portland cement type *III*/A spectra are well-separated from the rest, i.e. they are easy identifiable. The spectrum with lower concentration of calcium tends to end up further to the right of the plot, regardless of the differences between the different cement samples. The slag concrete spectra are most clustered and the cement spectra are moderately dispersed. The CaO spectra are spread out to the right of the plot. This behaviour may be attributed to the surface properties and different sample preparation methods. The slag concrete pellet with the binder maintains the best laser shot-to-shot repeatability, while the cement pellets without binder show a moderate repeatability. The porous calcium oxide powder produces dust which in turn causes fluctuations in the laser beam path that deteriorate the laser shot-to-shot repeatability. A dust suction device in the setup may resolve this issue.

Fig. 4. PCA score plot of the LIBS spectra collected for slag concrete, Portland cement types *I*, *III*/A, *III*/B and calcium oxide. Each material was spatially sampled by eight laser pulses, where each pulse delivered a spectrum.

Conclusions

It has been shown that Mg, Fe, Al, Cu, Ni, Pb alloys and CaO powder are distinguishable in 273 nm - 326 nm range using LIBS. Combined with PCA, LIBS is also an effective method to differentiate between slag concrete and Portland cement samples based on the Ca *II* emission lines. The different degrees of scattering and clustering in the score plot of PCA may be attributed mainly to different sample preparation procedures. It is desired to

also introduce different types of information to the PCA to increase its effectiveness, for example the FWHM, emission line quality factor and photon count ratios.

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