Laser-Induced Breakdown Spectroscopy (Libs) in Civil Engineering

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Abstract. Damage cases in concrete structures like pitting corrosion of the reinforcement from de-icing salts or concrete corrosion from aggressive sewage water require testing methods for reliable condition assessment of damaged structures and quality assurance of repair methods. LIBS as a tool for process control in steel and aluminium production was developed in the 1990ies. Testing of heterogeneous building materials like concrete has been developed at BAM in the last decade. LIBS application in civil engineering like imaging of element distributions, depth profiles of chlorides and sulphates or cement analysis will be described. Beside current applications LIBS has great potential for further applications.

Introduction

The Laser-Induced Breakdown Spectroscopy, LIBS, as a method for the element analysis on a solid, liquid, gas or aerosol surface has been developed since the 1980ies with more and more applications emerging since the 1990ies. Main applications are established in steel and aluminium production, on hot melts and waste sorting e.g. for aluminium, polymers, glass. Testing of heterogeneous building materials like concrete has been developed at BAM in the last decade. The LIBS equipment used for civil engineering applications is in principle portable and can be used on-site. Measurements can be performed directly on the sample surface and the results are available on-line.

1 Damage cases of concrete structures

The ingress of chlorides, e.g. from de-icing salts, leads to concentrated pitting-corrosion of the reinforcement with great risk for loss of stability (Figure 1a). To evaluate the consequences on stability and durability:

- The chloride content at the depth of the reinforcement has to be measured to decide if chloride-contaminated concrete has to be removed.
- A detailed depth profile of the chloride ingress has to be provided to deduce the chloride diffusion coefficient. Chloride diffusion coefficients allow the calculation of further ingress.

The ingress of sulphates or sulphuric acid constitutes are a major risk of chemical aggression for concrete. Progressive loss of strength and loss of mass caused by deterioration of the cohesiveness of the cement hydration products may occur (Figure 1b). External water-soluble sulphate compounds can ingress into the concrete, e.g. in sewage treatment plants or sulphate rich soils and damage the construction.


(a) (b)

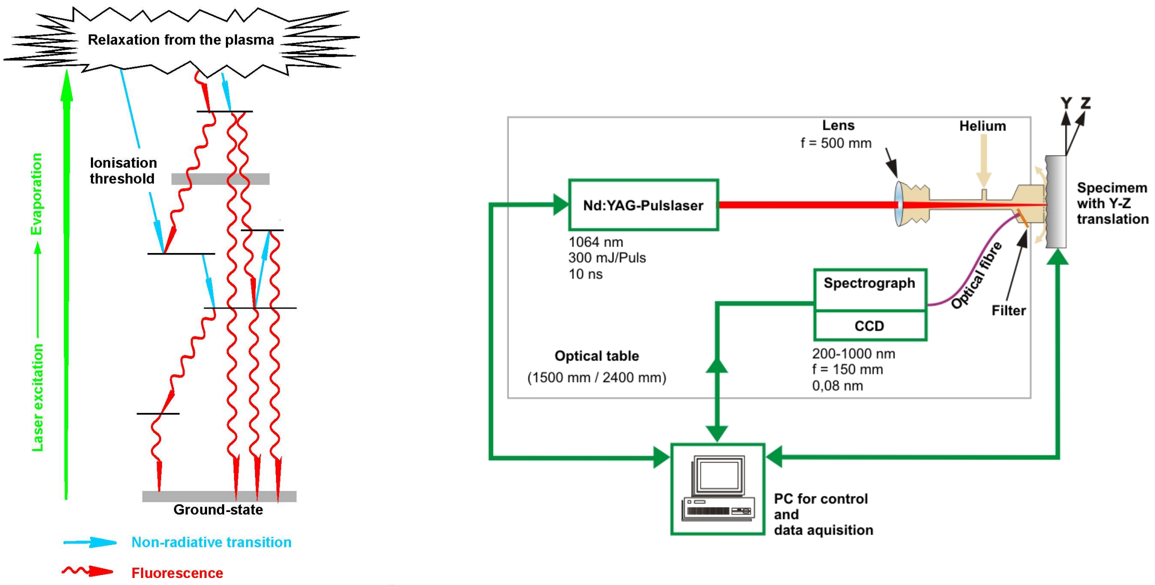
Figure 1 (a) Reinforcement steel with concentrated loss of section caused by pitting corrosion from de-icing salts. (b) Concrete corrosion with deterioration of the surface near concrete caused by sewage water in a sewage treatment plant.

2 Principle and measurement procedure of LIBS

For LIBS-investigations an intense laser pulse is focused on the surface of the specimen generating a plasma plume. During the relaxation process element specific radiation is emitted (Figure 2a). The radiation is guided through an optical fibre to the detection unit. The light intensity is measured as a function of the wavelength, i.e. the spectrum. Due to the high temperature in the plasma all chemical bonds are broken and atoms and partially ionised atoms are excited. Thus only information about elements in the evaporated mass is available. The content of the damaging species can be calculated directly from elemental content. The measurement of elements like chlorine and sulphur in concrete is a highly challenging task:

- The number of useful spectral lines that are not superimposed by lines of other elements is limited.
- The intensity of spectral lines of chlorine and sulphur is very weak compared with oxygen or calcium spectral lines.
- The natural heterogeneity of concrete requires a statistical evaluation of the results.

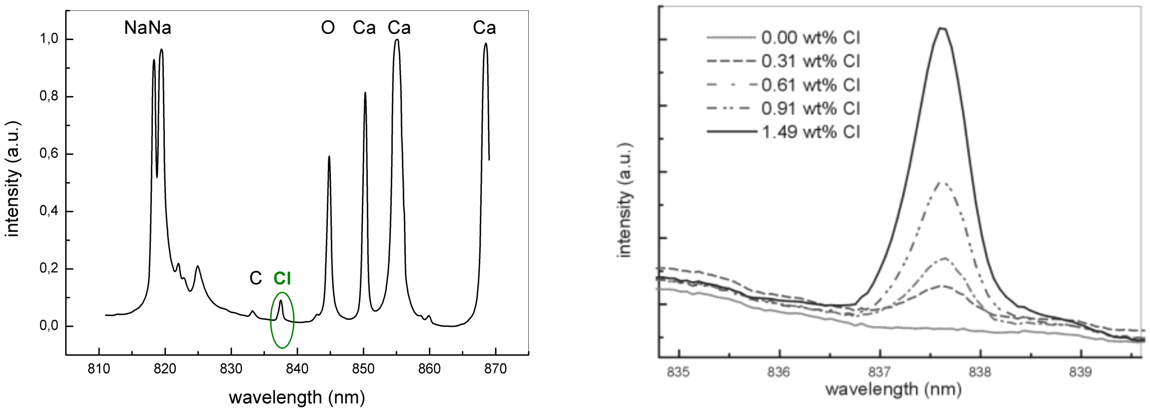
A typical LIBS experiment consists of a laser, an optical system focusing the laser beam onto the sample surface, a sample stage, an optical fibre guiding the light to the detection unit, and the detection unit consisting normally of a spectrometer and a CCD-camera. Optionally a gas inlet may provide a certain ambient atmosphere around the measurement region (Figure 2b).



(a) (b)

Figure 2 (a) Physical principle of LIBS. (b) Experimental LIBS set-up.

To evaluate the chloride content of a concrete specimen the chlorine spectral line at 837.6 nm is used for the quantitative determination of chlorine and stoichiometric conversion [1]. A spectrum measured on cement mortar is shown in Figure 3a. The total wavelength range was chosen from 811 nm to 869 nm. The spectrum provides a chlorine spectral line with good resolution and sufficient intensity. Also spectral lines from oxygen and calcium are included in the selected range. The peaks are marked with the element symbols. In Figure 3b the correlation between the intensity of the chlorine spectral line and the chloride content is shown. To deduce chloride contents from the measured chlorine intensity a calibration has to be carried out.



(a) (b)

Figure 3 (a) Typical spectrum measured in the wavelength region used for chlorine detection. The peaks are marked by the symbols of the elements. (b) Correlation between the intensity of the chlorine spectral line and the chloride content, measured on cement mortar samples.

With the same set-up it is possible to detect sulphur and to deduce the content of sulphates. The sulphur spectral line at 921.3 nm is suitable for sulphur detection in concrete. Systematic investigations with pure hydrated cement, mortar and concrete samples with varying sulphate content have been carried out at BAM and have been reported [2]. Also a linear correlation between the intensity of the sulphur spectral line at 921.3 nm and the sulphur content is found.

3 LIBS applications in civil-engineering

Damage assessment with LIBS has been successfully applied to concrete samples from bridge decks, parking garages and sewage treatment plants [3]. These structures are heavily exposed to concrete and reinforcement damaging de-icing salts (Figure 1a) and sulphuric acid (Figure 1b). To avoid loss of stability and to assess durability of a structure chlorine and sulphur content in the concrete are important properties to be measured. The results of LIBS measurement for chlorine and sulphur on different concrete members exposed to these aggressive conditions are presented. Furthermore a concept for LIBS used as a tool for quality assurance in the field of concrete repair will be introduced.

The progress that has been achieved compared with the presently state of the art will be presented like chlorine depth profiles in the mm-range compared with cm-range for standard chemical analysis. Element distributions can be imaged for an investigated surface. Thus, detailed information about the ingress characteristic of concrete damaging substances in the mm-scale becomes possible.

3.1 Imaging of element intensity

Concrete is a heterogeneous material of hydrated cement and aggregates. Every laser shot along the measuring grid produces a different spectrum. The results will be imaged colour-coded so that areas of aggregates, areas of mainly hydrated cement and concrete damaging substances like chlorides and sulphates are made visible.

(a) (b) (c)

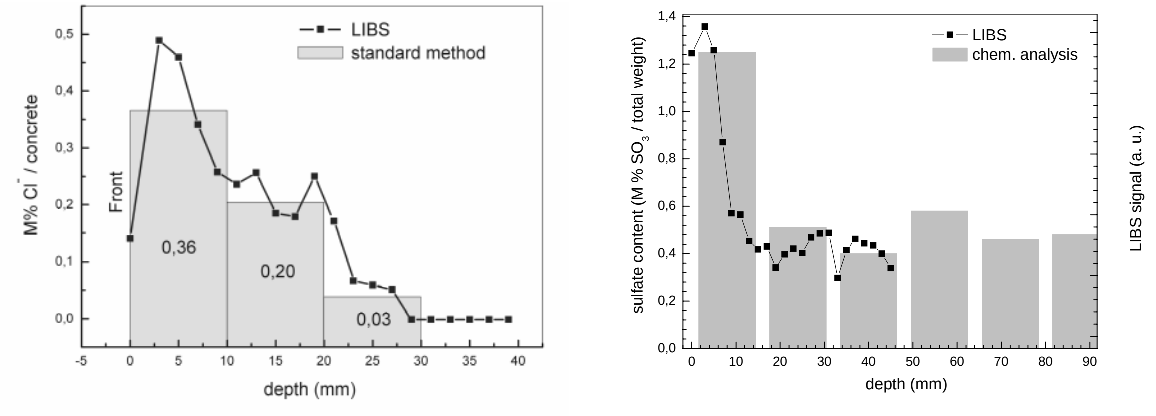
Figure 4 (a) Photograph of the split core. (b) Spatially resolved, colour coded imaging: black = aggregate, light colours = cement. (c) Spatially resolved, chloride distribution: white = evaluable chloride, black = absence of chloride).

Figure 4a shows a photo of the investigated concrete surface. Figure 4b shows the imaged calcium-oxygen-ratio for every position where a measurement was taken. Dark colours represent low ratios, i.e. aggregates; light colours represent high ratios according to a high intensity of the calcium spectral line, i.e. cement. A comparison with the photograph of the core shows a good agreement between the interpretation of the spectral features and the composition of the core. On Figure 4c the chloride content is visualised for each spot that was assigned to cement. If the chlorine spectral line is evaluated the spot is represented in white or light grey. If this is not the case, the pixel is represented in dark grey. It is obvious the chloride ingress is detectable with LIBS up to a depth of 25 mm. With the same procedure a concrete core from a sewage plant was investigated to measure the sulphate content.

3.2 Depth profiles

To characterize the ingress of chlorides and sulphates and to decide up to what depth contaminated concrete has to be removed detailed depth profiles of their content are needed. For the concrete cores depth profiles are available from the results introduced in section 3.1. The depth resolution follows from the distance of the line scans - 2 mm in case of the chloride measurement shown in Figure 5a. For each line scan at a certain depth the spectra belonging mainly to cement matrix were averaged. Values equal zero in greater depth of Figure 5a mean that no evaluable chlorine spectral line was detected. Chloride contents could be determined down to approx. 0.03 wt% chloride related to concrete. This comes up to a calculated value of 0.2 wt% chloride related to cement. The first value at 0 mm depth was measured on the surface of the front side.

The depth profile in Figure 5a shows the expected characteristic of chloride ingress with the maximum peak a few millimetres below the surface. The higher depth resolution compared with the results of the standard chemical analysis allows deducing a reliable chloride diffusion coefficient. With this parameter the further chloride ingress can be calculated.



(a) (b)

Figure 5 (a) Depth profile of chloride ingress, measured with LIBS on a core of an offshore building compared with standard chemical measurements [1].
(b) Depth profile of sulphate ingress, measured with LIBS on a core of sewage plant compared with standard chemical measurements [2].

The practical use for a detailed chloride depth profile like shown in Figure 5a is to determine up to what depth chloride contaminated concrete has to be removed. This first step in quality assurance is to guarantee a durable concrete repair. The second step is to control on-site if the removal of the concrete was sufficient. A LIBS-on-site device to determine the remaining chloride content at the prepared concrete surface is under development at BAM. Large areas such as bridge surfaces could be tested and further removal could be immediately instructed if necessary.

The practical use for a detailed sulphate depth profile like shown in Figure 5b is to find out up to what depth sulphates from an external source are present and if there is a risk for later debonding of shotcrete due to expansive reactions of sulphur components in the boundary of old concrete and shotcrete.

References

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