Laser Induced Breakdown Spectroscopy (LIBS) – alternative to wet chemistry and micro-XRF

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Abstract
The laser induced breakdown spectroscopy (LIBS) gives an alternative to the standard techniques for the direct investigation of a building material. It utilize a high energy pulsed laser beam for ablation and vaporization of a small amount of material, a plasma is formed and the plasma radiation is investigated using optical emission spectroscopy. Due to the principal all elements are detectable during one measurement. In combination with a translation stage or scanner system the heterogeneity of concrete is considered in the results. Thus an element concentration may be correlated to the cement content. After calibration with a set of reference samples quantitative results are obtained. The system is automated and allows rapid measurements and minimizes the possibility of errors. At BAM a laboratory LIBS system has been successful applied for the investigation of transport processes of different ions in building materials. The spatial resolution of the measurement may rich 100 µm and the frequency of the measurements is 100 Hz. The concentration of chlorine, sulfur, carbon, sodium, potassium, lithium and hydrogen where quantitatively determined. A mobile system for on-site analysis on bridges or parking decks is available. It is a tool for the estimation of the condition of concrete structures and for quality assurance during concrete repair work on-site. In these work an overview of the possibilities of LIBS for automated investigation of building materials are given.

Keywords: LIBS, elemental analysis, heterogeneity, chlorides, sulfates, alkalis, corrosion, ASR, carbonation

1. Introduction
Reinforced concrete structures are designed in consideration of a specific expected lifetime of approximately 50 years. Due to environmental influences and moisture ingress through the pore system often combined with ingress of harmful ions damage-processes due to deterioration of concrete and/or reinforcement may occur.

Laser induced breakdown spectroscopy (LIBS) can be applied as a fast and reliable method directly on the optical accessible surface (cross section of a concrete core) in order to identify harmful species and their accompanying damage processes. Transport processes in concrete like diffusion and migration may be investigated. In principle all elements are detectable during one measurement. In combination with a scanning technique the heterogeneity of the material is taken into account by separating measurements taken on aggregates and measurements taken on cement-matrix. This is done by evaluating the ratio of different elements during one measurement. As an example a high sodium concentration in aggregates may be distinguished from the sodium ingress via transport-processes which occur in the cement-matrix via pores. Also ion transport in damaged concrete due to cracks may be measured. A typical measurement records quantitative element concentrations on an area of 80 mm x 100 mm with a resolution of 0.5 mm in 10 minutes. At the same time chlorine (chlorides) and carbon (carbonation) are measured. Only minor sample preparation is necessary. The measurement are performed under normal conditions, vacuum is not needed. Even light elements like hydrogen or sodium are detectable. Using reference samples for calibration purposes the results may be quantified.
LIBS is a fast developing technique with applications in different fields like environmental analysis, pharmaceutical investigation, biomedical investigation, forensic investigation or industrial applications like process control, recycling, sorting and quality control during manufacturing [1, 2]. At BAM LIBS has been successfully applied for laboratory investigations of 2-D element concentrations for chlorine, sulfur, carbon, sodium, potassium, lithium and hydrogen. Also transport-processes in building materials [3-7], the identification of substances and the evaluation of quantitative ratios by means of an integrated marker are demonstrated [7].

In cooperation with system developers and companies a mobile LIBS-system was tested during on-site measurements by BAM.

2. Experimental setup

For investigations on concrete samples in the laboratory a pulsed NdYAG laser (Innolas Spitlight 600) with an output energy of 350 mJ per pulse is used at fundamental wavelength of 1064 nm at a frequency of 10 Hz. The laser beam is expanded by a beam expander and then focused on the sample surface with a lens (f = 50 mm). The spot size of the laser focus at the sample surface is 0.2 mm. The light emitted from the plasma is guided by an optical fiber. The fiber is coupled to the entrance slit of a Czerny-Turner type spectrometer (Shamrock 303i). A grid with 1200 lines per mm was used for the detection in the near infrared section (NIR) of the spectrum. In front of the entrance slit of the spectrometer an edge filter suppress light with wavelength below 550 nm is located. A CCD (Andor Idus DV420 BR-DD) with high quantum efficiency in the NIR is used as detector. The NIR region of the spectrum was chosen because there are sensitive lines of chlorine, sulfur, sodium, carbon and also lines which may be used for the evaluation of heterogeneity.

Figure 1. Translation stage with concrete core. View on cross section obtained by dry cut. The specimen is moved during the measurement line by line in the plane perpendicular to the laser beam.

The specimen under investigation is located on a translation stage and may be moved in a plane perpendicular to the laser beam. To remove dust and to get a lower limit of detection especially for chlorine the environment of the plasma is purged with helium.
3. Measurement

For LIBS measurements only an optically accessible surface is necessary. To get volume information, a core has to be cut in the middle. This is done by dry cutting or by cutting cooled with petroleum. The measurements are performed on the cross section of the core (figure 1). For LIBS measurements with the lab-system the sample is placed on the translation stage at a constant distance to the lens. The sample is scanned line by line. Standard measurements are made, depending on the issue, with line spacing between 0.25 mm to 2.0 mm. The interval of subsequent measurements per line is also of the same order. Using this scanning technique the heterogeneity of concrete is recorded. The resolution of a measurement is a compromise between exact reproduction of material heterogeneity and time for a measurement. The higher the resolution is chosen the more time is needed for the measurement. The set-up is controlled by a laboratory-written LABVIEW software. An automated measurement procedure minimizes the liability to errors and enables fast analysis of samples.

4. Results (ASR)

The alkali-silica reaction (ASR) may cause the de-generation of highway structures starting with crack formation and later spalling of the concrete surface. In Germany hundreds of kilometres of highways are potentially effected, which causes severe restriction in traffic and the need of extensive funds for reconstruction. ASR is initiated if reactive aggregates, alkalines and water are present in the concrete. One source of alkalines, in most cases sodium, is the de-icing salt used extensively during winter time in the last decades. With LIBS it is possible to detect the ingress profiles of sodium. These can be used to estimate the endangering of highways and also to evaluate the effectivity of performance tests used to evaluate aggregates.

![Figure 2](image-url)

**Figure 2**, Photo of cross section of a concrete core (a), evaluation of sodium concentration in the core (40 mm x 70 mm) by LIBS (b). The sodium content is marked by blue color. Brighter blue means higher sodium concentration. Comparison of µXRF (c) and LIBS (d) results (aggregates are excluded and marked by black color).

One technique available in laboratories to investigate building materials is µXRF. This technique works well to measure ingress profiles of chlorine. But for lighter elements like starting with sodium the sensitivity is, due to the principle, limited. In contrast LIBS is sensitive for sodium detection (see figure 2b). Both methods may in principle consider the heterogeneity of the material. In figure 2 a
comparison of evaluation of sodium concentration in a concrete core by µXRF (2c) and LIBS (2d) is presented. The aggregates are excluded and marked by black color. The sodium content is marked by blue color. More intensive blue means higher sodium concentration.

![Graph](image)

Figure 3. Comparison of ingress profile of sodium measured on the cross section of the concrete core shown in figure 2a. Blue curve obtained by consideration of all measurements (2b). Red curve obtained by excluding measurements on large aggregates (2d).

Only in the LIBS results the sodium ingress due to the pore system of the cement matrix can be seen. The heterogeneity of concrete is considered and the sodium content in the aggregates is excluded. The sensitivity of µXRF for the measurement of the sodium concentration is not sufficient.

5. Conclusions

The following conclusions may be drawn from the investigations exemplarily shown above:

- LIBS is able to measure directly on the sample surface. An optimum sample drawing is given.

- The method is able to measure the heterogeneity of the material. The measured ingress profile of sodium is correlated with the cement matrix.

- LIBS is able to detect light elements which may be difficult by XRF.

- LIBS is allows fast and automated measurements with savings time and man power.

References


