



Determination of chlorine, sulfur and carbon in reinforced concrete structures by double-pulse laser-induced breakdown spectroscopy



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ABSTRACT

Accurate and reliable quantitative determination of non-metal corrosion agents in concrete is still an actual task of analytical use of LIBS. Two double-pulse LIBS systems were tested as a tool for the determination of chlorine, sulfur and carbon in concretes. Both systems had collinear configuration; a laboratory setup was equipped with an ICCD and two lasers (355/532 nm + 540 nm), but a CCD was a detector for a mobile system with one laser (1064 nm). Analytical lines of Cl I at 837.59 nm, S I at 921 nm and C I at 247.86 nm were used to plot calibration curves. Optimal interpulse delays for the laboratory setup were 4 μs for chlorine and 2.8 μs for carbon, while an interpulse delay of 2 μs was optimal for chlorine and sulfur determination with the mobile system. We suggested the normalization of the Cl I line at 837.59 nm to the Mg II line at 279.08 nm (visible at 837.23 nm in the third order) to compensate for pulse-to-pulse fluctuations of chlorine lines. It provided the decrease of the detection limit of chlorine from 400 ppm to 50 ppm. Therefore, we reported that LIBS can be used to determine main corrosive active substances under ambient conditions in concrete below critical threshold values. Moreover, the application of the mobile system for in-situ qualitative assessment of corrosion way of a steel cage of a swimming pool dome was also demonstrated. It was found that chloride corrosion due to the disinfection of water was the main way for corrosion of the open part steel and the steel rebar inside the concrete.

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1. Introduction

Chemical degradation of concrete has remained a serious problem in the construction industry for decades. As a rule, reinforced concrete structures are in contact with an atmosphere, water, or ground. These environments contain substances which can modify the chemical composition of its pore solution. Despite the relative chemical stability of concrete compared to the other major components of reinforced structures, there are still many diverse forms of chemical attack that must be dealt with, such as corrosion of reinforced steel (especially, chloride corrosion), carbonation, and sulfate attack [1].

Chlorides are dissolved in water and penetrate with it into concrete, either by the wetting of a non-saturated concrete or by diffusion, because the chloride content is higher in the environment than in the original concrete. Sulfate attack typically occurs where water containing dissolved sulfate penetrates the concrete. Carbon dioxide can be absorbed by the concrete pore solution from the ambient atmosphere, and form calcium carbonates (carbonation), and, as a consequence, the pH is decreased to about 10 for the pore solution of carbonated

concrete [2], resulting in loss of the passivation ability of cement stone related to steel reinforcement [3].

To quantify the risk of a chloride presence in concrete the critical threshold of chloride content is often used. It is usually expressed as a total chloride content relative to the weight of the cement. The main reason for this is the fact that the determination of a total chloride content is described in various national standards [4–6]. Besides classical chemical techniques with dissolution of concrete stone in nitric acid, X-ray fluorescence attempted to be used for chloride content determination. However, chloride fluorescence intensity is greatly reduced at the same concentration level when chloride is present in the concrete matrix as NaCl salt instead of being dissolved in a pore solution and is influenced by grain size. These resulted in large systematic errors of chloride content determination by XRF [7]. At the same time, micro-XRF can be used to study the relative spatial distribution of chloride [8]. Thereby XRF determination of chloride in concrete reduces to a case where a number of measurements on the same samples are needed. As for chlorides the standard methods of the sulfate determination in cement and concrete after its dissolution in hydrochloric acid are laboratory chemical analyses like ICP-AES or gravimetry. The simplest way to characterize the carbonation is the use of the indicator phenolphthalein for pH decrease detection. Therefore, this is an indirect qualitative technique for carbon determination in concrete. Quantitative

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measurements to determine total carbon calculated as carbon dioxide are the following: loss on ignition, thermogravimetric analysis, and combustion by induction furnace with detection by IR-absorption. Thus, simultaneous determination of elements responsible for the main types of chemical attacks on the concrete, especially in field conditions is difficult, since common techniques require different kinds of sample treatment and analytical methods.

It was shown that laser-induced breakdown spectroscopy (LIBS) is the cost-effective technique for remote detection of non-metals in the mining industry [9]. In recent years, the elemental analysis of building structures with the use of LIBS has been also actively developed [10, 11]. LIBS is a rapid analytical technique based on the creation of a laser plume on the surface of any material by high-power pulsed laser radiation. The emission of evaporated and atomized material in laser plasma provides qualitative and quantitative information on the sample composition [12]. The main advantages of LIBS for diagnostics of building materials are: (i) the capability for simultaneous determination of all elements; (ii) relatively simple apparatus (in particular, no vacuum requirement), which allows miniaturization and automation of the analytical measurements in the field; (iii) high throughput; and (iv) local analysis.

The possibility for the characterization of changes in the structure of construction materials due to corrosion, caused by atmospheric interactions, with the assistance of LIBS was demonstrated by Wilsch et al. in 2005 [13]. Firstly, this LIBS method is not sensitive enough for the determination of non-metals (chlorine, carbon, and sulfur) which are responsible for the degradation of concrete. However, figures of merit of concrete elemental analysis were found to be insufficient for a wide application of this method and a further improvement is preferable to reduce the limit of detection for Cl in concrete [14,15]. The basic complications in determining non-metals in concrete are the high excitation potential and the low atomization level of the elements in the plasma. Therefore, for the excitation of non-metals, hotter and more dense laser plasmas are used, for example, double-pulse operation with orthogonal scheme [16] or additional excitation by electrical discharge [17]. In these cases, detection limits were lowered to 80 and 500 ppm, respectively. Both of these solutions significantly complicate mobile LIBS systems, which realize the main advantages of the technique compared with conventional methods of concrete chemical analysis. At the same time chlorine determination at the level of hundreds of ppm is required because the most conservative estimate of the corrosion threshold for conventional reinforcement is 0.6 kg/m³ (~300 ppm) [18], and temperature growth from 20 to 70 °C causes a 5-fold reduction in the threshold level [19]. Analytical LIBS measurements of concrete composition under helium flow provided a sufficient limit of detection for sulfur for the LIBS application [20], and can provide sulfur distributions and millimeter resolved depth profiles to study sulfate ingress

into concrete [21]. Kagawa et al. [22] demonstrated that LIBS is appropriate as an in situ quantitative method of inspection for carbonation of concrete by measuring of the total carbon content in concrete. They compared Nd:YAG and TEA CO₂ lasers and concluded that signal-to-background ratio is not applicable for the spectrochemical analysis in the case of an Nd:YAG laser. Thus, well-known techniques of determination of chlorine, sulfur and carbon by LIBS need helium flow or the use of bulky lasers, which limits LIBS diagnostics of degradation of concrete in the field work. It is still important to develop approaches suitable for mobile LIBS, to enhance the determination of the abovementioned non-metals in concrete in the air.

2. Experimental

2.1. Laboratory setup

Two systems were built to examine the possibilities of LIBS for determination of non-metals in concrete. The laboratory setup in the Laser Diagnostics Laboratory of Moscow State University was thoroughly described in our previous work [23]. The main operating parameters of lasers, spectrograph, and ICCD are listed in Table 1. Beams of two independent lasers went onto the polarizing beamsplitter cube and had the same optical way after it through the mirrors and an achromatic doublet pair ($f = 150$ mm) focused both beams into the same point. To avoid pre-breakdown on aerosol particles produced on concrete samples a focus of doublet pair was placed below 5 mm from a sample surface. Since beam divergence and transverse mode structure were differed for lasers (see Table 1), the doublet pair produced spots sufficiently different in size: the first laser gave a spot of ~150 μm, but the second laser produced a spot of ~500 μm. A set of samples simulating concretes with the different contents of chlorine, sulfur and carbon were prepared in the Laser Diagnostics Laboratory (further, MSU samples) to assess the capabilities of the laboratory setup for the determination of non-metals. Raw material was a Portland cement M500 (ZAO "Cementtorg", Russia) in accordance with GOST 10178-85. We added chlorine, sulfur and carbon in the form responsible for degradation processes. Solutions of SrCl₂ × 6H₂O (analytical grade), Na₂CO₃ (analytical grade) and Na₂SO₄ (analytical grade) were prepared as an addition to the cement powder. 15 g of cement powder was placed into a Teflon cup to mix with 6 mL of deionized water. Then the calculated volume of the additions was placed into the cup, and the wet powder was thoroughly stirred. A cup was weighted before and after stirring to take into account a loss of cement porridge on a spatula. After the last weighting, a mixture was kept in air for several days until a mass of a cup with concrete sample did not change within an error of 0.1 mg. The content of chlorine, sulfur and carbon in the prepared materials was changed in the range of 0.05–1.5%. A set of concrete

Table 1
Main parameters of both setups.

Parameters	Laboratory set-up		Mobile set-up
Laser	Nd:YAG (1st laser)	Nd:YALO (2nd laser)	Nd:YAG
Wavelength (energy per pulse)	355 nm (10–70 mJ)	540 nm (70 mJ)	1064 nm (55 mJ)
Pulse duration	<8 ns	20 ns	8 ns
Beam diameter	6 mm	6 mm	4 mm (after telescope 12 mm)
Beam divergence	<0.8 mrad	6 mrad	1.5 mrad
Pulse repetition	5 Hz	5 Hz	Up to 10 Hz
Stability of energy per pulse	<2%	<4%	<2%
Spot size, μ	150	500	100
Position of focus below surface, mm	5		2
Spectrograph	Czerny–Turner		Czerny–Turner
Slit	25 μm		
Focal length	320 mm		200 mm
Grating	1800 lines/mm, 68 mm × 68 mm		3 gratings
Resolution	8000 (at 400 nm)		
Aperture ratio	1:4		1:3.6
Intensifier	Multialkaline, Ø 18 mm, gain 1–50,000		–
CCD size	1040 × 1390 pixels, 6.5 μm × 6.5 μm		3648 pixels or 2048 × 64 pixels

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