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Quantitative estimation of carbonation and chloride penetration in reinforced concrete by laser-induced breakdown spectroscopy

Shuzo Eto [a,*], Toyofumi Matsuo [a], Takuro Matsumura [a], Takashi Fujii [a], Masayoshi Y. Tanaka [b]

[a] Central Research Institute of Electric Power Industry, 2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan
[b] Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan

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ABSTRACT

The penetration profile of chlorine in a reinforced concrete (RC) specimen was determined by laser-induced breakdown spectroscopy (LIBS). The concrete core was prepared from RC beams with cracking damage induced by bending load and salt water spraying. LIBS was performed using a specimen that was obtained by splitting the concrete core, and the line scan of laser pulses gave the two-dimensional emission intensity profiles of $100 \times 80\ mm^2$ within one hour. The two-dimensional profile of the emission intensity suggests that the presence of the crack had less effect on the emission intensity when the measurement interval was larger than the crack width. The chlorine emission spectrum was measured without using the buffer gas, which is usually used for chlorine measurement, by collinear double-pulse LIBS. The apparent diffusion coefficient, which is one of the most important parameters for chloride penetration in concrete, was estimated using the depth profile of chlorine emission intensity and Fick's law. The carbonation depth was estimated on the basis of the relationship between carbon and calcium emission intensities. When the carbon emission intensity was statistically higher than the calcium emission intensity at the measurement point, we determined that the point was carbonated. The estimation results were consistent with the spraying test results using phenolphthalein solution. These results suggest that the quantitative estimation by LIBS of carbonation depth and chloride penetration can be performed simultaneously.

1. Introduction

Reinforced concrete (RC) is used in a large number of infrastructure buildings and basements. Chloride-induced damage and neutralization of RC are the main causes of degradation of the reinforcing bar in RC. In coastal areas, salt particles attach to the surface of the RC structure and penetrate into the concrete. The reinforcing bars in the RC become eroded when the chloride in the salt particles reaches them. The chloride-induced damage depends on the cracking of the RC surface because the salt particles penetrate more quickly into the concrete with cracking damage than into that without cracking damage. Although many experimental studies on the relationship between the crack width and the penetration depth of chloride have been performed [1], no relation has been established. The depth profile of the chloride concentration in concrete provides fruitful information on the effect of the presence of cracks on the chloride penetration. The neutralization of the concrete, in which the alkaline pH of the concrete changes into neutral pH, also affects the erosion of the reinforcing bar in RC. The pH change occurs according to the following scenario. First, the carbon dioxide in the atmosphere penetrates into the concrete. Second, the fraction of the calcium carbonate increases in the concrete owing to the chemical reaction between carbon dioxide and calcium hydrate in the concrete. Finally, the increase in the calcium carbonate concentration induces the change in pH. If the neutralization of the concrete occurs around the reinforcing bar, the reinforcing bar is easily eroded because the passivity of the reinforcing bar disappears. Therefore, the depth of the neutralization is an important information on the erosion of the reinforcing bar. The neutralization of concrete also affects the chloride penetration in the concrete because the neutralization causes the dissolution of Friedel's salts, which are stabilized in the cement, into the chloride ions that move to deeper positions of the concrete [2]. The methods of estimating the chloride penetration or neutralization in concrete are important for investigating the complex degradation mechanisms of RC.

In general, the measurement of chlorine concentration in concrete has been performed by standard chemical methods using potentiometric titration (PT). However, PT requires the preparation of the concrete sample for the concentration measurement, which takes a long time. Laser-induced breakdown spectroscopy (LIBS) is an attractive tool for the fast measurement of elements in the concrete. LIBS of chlorine in concrete has been performed, and the results show that the use of helium buffer gas [3,4], double-pulse (DP) configuration [5–7], measurement under reduced pressure [8], and combination of laser pulse

* Corresponding author. Tel.: +81 46 856 2121; fax: +81 46 856 3540.
E-mail address: eto@criepi.denken.or.jp (S. Eto).

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and electric spark [9] are effective for enhancing the emission intensity of chlorine. To use LIBS for on-site measurement, the omission of buffer gas is one of the key issues. In particular, DP LIBS allows a compact setup for enhancing the chlorine emission intensity without the vacuum device, gas container, and other devices.

The detailed analysis of the chlorine penetration is ordinarily performed using an electron probe microanalyzer (EPMA). Although EPMA gives the two-dimensional profile at the surface of the concrete with high spatial resolution of micrometer order, accurate measurement requires a sample with a flat surface because the fluorescence X-ray intensity depends strongly on the roughness at the surface of the measurement area owing to the attenuation length change of the fluorescence X-ray emitted from the inside of the specimen. Therefore, a sample with a rough surface such as the RC with cracking damage cannot be measured using EPMA. In addition, EPMA requires a vacuum chamber for measurement. LIBS and X-ray fluorescence (XRF) are candidates for on-site measurement of elements in RC. XRF is effective for simple examination for the detection of elements and semi-quantitative measurement by the fundamental parameter method. Samples with rough surfaces cannot be measured by XRF owing to the same reason as in the case of EPMA. In addition, it takes several dozen seconds to measure one point because the fluorescence X-ray intensity is weak. LIBS gives two-dimensional profiles of elements in RC with a spatial resolution lower than that of EPMA. However, the fast measurement of a large sample is possible because the bright emission spectrum is measured by single-shot irradiation of a laser pulse. Some reports show that the two-dimensional measurement of chlorine emission intensity by LIBS gives the detailed penetration profiles in the concrete [3,10]. Samples with small roughness can be measured by LIBS, but there are few reports concerning the measurement of the concrete with cracking [11].

The measurement of the neutralization depth of concrete is usually performed by spraying phenolphthalein and verifying the color change at the concrete surface. Although the method can be used to easily measure the neutralization region from pH 8 to 10, the pH cannot be measured. If the equivalent pH can be measured, the neutralization depth can be measured precisely. Kagawa et al. measured the carbon emission intensity by LIBS to estimate carbonation in mortar [12]. However, the carbonation of the concrete was not estimated.

In this study, two-dimensional simultaneous measurements of multiple elements in the RC core with cracking and chloride-induced damage were performed by single-pulse (SP) LIBS with helium buffer gas or DP LIBS without buffer gas. In addition, the effect of the presence of cracking on the emission intensity was discussed on the basis of the measurement results of the RC with the cracking damage. The carbonation depth was estimated by a statistical approach. The presented methods and data processing can provide a fast, on-site measurement method of the penetration profile of chlorine and the neutralization depth of concrete.

2. Experimental setup

2.1. Materials

RC core samples of 100 mm diameter, picked out from the RC beams, were used for the LIBS. The geometry of the RC beams is shown in Fig. 1. The diameters of the main reinforcement and shear reinforcing bar were approximately 16 and 6 mm, respectively. The covering depth of the main reinforcement was 32 mm. Ordinary Portland cement was used for the RC beams. The compositions of the concrete are shown in Table 1. To produce the chloride-induced damage and cracking damage, the RC beams were subjected to two types of deterioration test [1]. First, the RC beams were subjected to the four-point bending test to induce the cracking at the surface of the RC beams. Second, the RC beams with cracking damage were placed in a room with a constant temperature of 40 °C and a relative humidity of 90%. Third, a solution of sodium chloride was sprayed on the surface with the cracking once every two days. Finally, the RC beams were again subjected to the four-point bending test to yield the main reinforcement. The deterioration levels of the RC beams are shown in Table 2. The four-point bending test of beam 1 or 2 was stopped just after the yield of the main reinforcement or that with the local crash of concrete, respectively. Finally, the RC cores were picked out from the RC beams. The cores were split into two pieces, and their cross sections were measured by LIBS. In this study, we call the split core, picked out from beam 1, Core 1, and those from beam 2, and Cores 2 and 3. One of the cores was used for the LIBS; the other was used for the chemical analysis by PT.

2.2. Experimental setup for LIBS

The experimental setup for LIBS is shown in Fig. 2. Second-harmonic Nd:YAG lasers (Hoya, Continuum, Powerlite 8010) operating at a repetition rate of 10 Hz were used. Two types of LIBS configuration were used in the experiments as shown in Fig. 2. For the measurement of Core 1, the output pulse of laser 1 was irradiated perpendicularly to

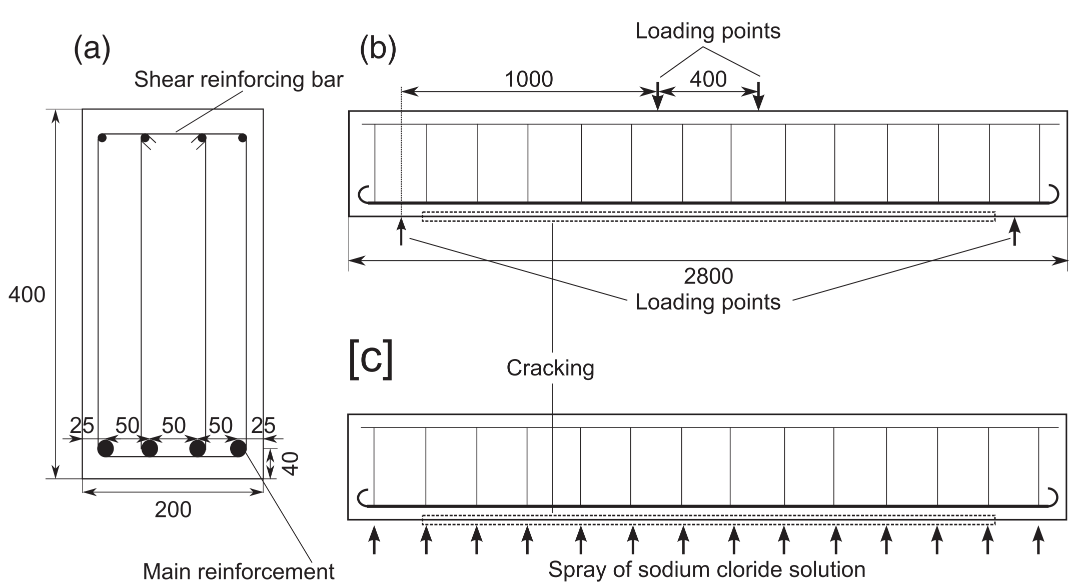

Fig. 1. Schematic of reinforced concrete beam from (a) side and (b), (c) front. (b) Loading test. (c) Salt spray test. The loading test was conducted before the salt spray test. Thick and thin lines indicate the main and shear reinforcement bars, respectively. Unit in the figure is mm.