Chloride ingress in cracked concrete studied using Laser Induced Breakdown Spectroscopy

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Abstract: Cracks are always present in reinforced concrete structures. It is a goal of the current research to study the influence of mechanical cracks on chloride ingress. A compact reinforced concrete specimen was designed, mimicking the cracking behaviour of beam elements. Cracks of different widths were induced by means of mechanical loading. These cracked specimens were then subjected to 45 weekly cycles of wetting and drying with NaCl solution. After the exposure, the specimens were cut, and chloride profiles determined using Laser Induced Breakdown Spectroscopy (LIBS), an innovative technique which enables simultaneous determination of different elements with high spatial resolution and minimal specimen preparation. Combining different element distributions, it is possible to discriminate between coarse aggregate particles, and the mortar matrix.

Keywords: chloride ingress, concrete cracking, LIBS

1 Introduction

Chloride induced reinforcement corrosion is a common deterioration mechanism affecting reinforced concrete structures. Structures built in marine environments and those exposed to action of de-icing salts in the winter are especially vulnerable. Even worse, these structures need to maintain their durability under combined action – under structural loading and chloride exposure. In reinforced concrete structures, it is expected that a certain amount of cracking occurs under load.

Cracks are virtually inevitable in reinforced concrete structures. Once formed, they present fast routes for transport of aggressive substances into concrete. Because of this cracks are preferential routes for chloride ingress. It is therefore essential to determine to which extent cracking influences chloride penetration.

In the past two decades several researchers have investigated the effect of cracking on chloride ion penetration in concrete (e.g. [1-4]). For a comprehensive review of these studies, see [5]. However, due to different experimental conditions and techniques used in these studies, there is still no consensus on the influence and importance of cracking on chloride penetration. One of the issues is that most studies use plain concrete specimens, as opposed to using reinforced concrete. However, reinforced concrete has somewhat different cracking behavior than plain concrete. As tension occurs in the reinforcing steel, microcracks form in the steel/concrete interface. Also, debonding of the steel/concrete interface occurs, possibly creating a fast pathway for fluid penetration. This was proven in an investigation by Wittmann et al. [6], who non-destructively monitored water penetration in reinforced cracked specimens using neutron radiography. Rapid moisture penetration along the damaged steel/concrete interface was observed. Pease [4] also found that damage created in the steel/concrete interface could be more detrimental to chloride ingress and subsequent steel corrosion that cracking of the concrete cover itself.

In this work, chloride ingress in cracked reinforced specimens is studied using an innovative experimental technique, namely Laser Induced Breakdown Spectroscopy (LIBS) [7-8]. Using LIBS, two dimensional distributions of chloride and sodium in concrete specimens are obtained and analyzed.

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2 Materials and methods

2.1 Materials and mix design

Cement used in this research was ordinary Portland cement CEM I 52.5 R. Water to cement ratio of the mix used was 0.45. Super plasticizer was added to increase the workability of the mix. The composition of the fabricated specimens was: cement content 380 kg/m^3; fine aggregate (<4mm) 1027 kg/m^3; coarse aggregate (>4mm up to 12mm) 840 kg/m^3; super plasticizer 1.4% wt. cement. The mixing procedure was the following: first, fine aggregates (0-4 mm) were dry mixed for one minute; then cement was added, and mixing continued for an additional minute. Then, the water containing dissolved super plasticizer was poured into the mixer. After this, the mortar was mixed for four minutes, then stopped and remained still for one more minute. The mixing was resumed and the coarse aggregate (4 to 16 mm) was added. Finally, the complete mix was mixed for 5 more minutes. The total mixing time was 10±1 min. The air content of the mix was determined in fresh condition and was 3.1%. The average compressive strength of hardened concrete (on standard cubes with side length of 150 mm) measured on 3 specimens after 28 days was 55.4 MPa. For this, three standard concrete cubes (150x150x150 mm^3) were cast. All specimens, including the strength specimens, were demoulded after 24 hours. Then, they were stored in a climate (fog) room at 20±2 ˚C and more than 95% relative humidity for 28 days.

2.2 Specimen preparation

A modified wedge-splitting method has been selected. The wedge-splitting method has been developed by Brühwiler and Wittmann [6] to determine fracture properties of concrete, such as fracture energy and toughness. A specimen is prepared by casting or sawing a groove and a notch. In the testing machine, the specimen is placed on a linear support. Two rollers and a wedge are used to transfer the vertical load (i.e. machine movement) into horizontal load. Two LVDTs are placed at the bottom of the notch, and their average is used as a feed-back signal to the machine. This way, the average crack width is controlled. Compared to the original wedge-splitting test [6], the specimen geometry used herein is modified by inserting two reinforcement bars.

For the specimen preparation, cubic moulds of 150x150x150 mm^3 are used. Inside the mould, two reinforcing bars of 12 mm diameter and about 120 mm in length are placed (Figure 1). Prior to casting the specimens, a PVC profile with a cross section of 40x40 mm^2 is mounted on the mould, in order to create a recess. This PVC profile is removed around 2 hours after casting. This way, the desired specimen geometry is obtained.

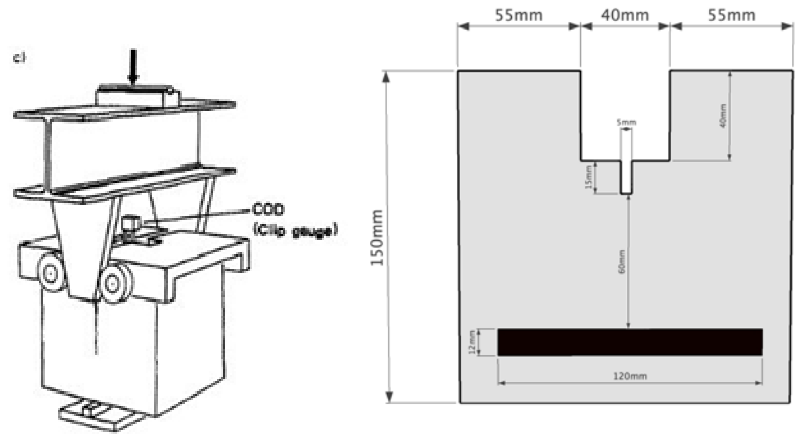


Figure 1 Setup of the wedge-splitting test [6] (left) and specimen geometry used in the modified test (right)

After the curing period, a notch (5 mm thick) is sawn in the specimen using a water cooled saw. The purpose of the notch is to guide the fracture process; namely, the crack should typically start

from the notch. The depth of this notch can also be adjusted in order to achieve certain concrete cover depth. It should not be too shallow, however, since the crack then might initiate outside the notch.
Wedge-splitting specimens were taken out of the climate chamber after 28 days and thereafter stored at room temperature until testing. At the age of 36 days, cracking procedure was performed. In order to control the obtained crack width, LVDTs are placed on both sides of the specimen at the bottom of the notch, where the crack is expected to initiate. Their average is used as a feed-back signal for the machine, and controls the whole loading process. In this way, a stable cracking procedure is performed.

After cracking, the specimens were exposed to 45 weekly salt-dry cycles consisting of 48 hours of 3.3% NaCl solution contained in the recess and 5 days of drying at 20 C and 50% RH. The solution was poured in a pond formed by the recess and two rubber sheets glued to the sides of each specimen. At the end of the exposure to chlorides, the specimens were cut into three pieces parallel to the rebars, with two side pieces containing a rebar each. The middle piece was analyzed using LIBS.

2.3 Laser Induced Breakdown Spectroscopy (LIBS) technique

Laser induced breakdown spectroscopy (LIBS) is a powerful and reliable optical technique for the detection of trace elements present in a solid and liquid sample [7]. It is a sort of atomic emission spectroscopy where analyses are performed by monitoring intensities and wavelengths of the emission lines. A highly energetic laser pulse is focused to form a plasma on the surface of the specimen. The plasma excites and atomizes the specimen, and the atomic emission spectrum is recorded. In principle, all elements can be detected by LIBS, since all elements emit characteristic frequencies when excited to sufficiently high temperature. In practice, this is limited by the power of the laser, sensitivity and wavelength of the detector and the spectrometer. Compared to wet chemical analyses, specimen preparation for LIBS is simple. A split or cut concrete surface is examined, and no grinding/crushing of concrete is needed. Also, multiple elements can be traced with a single LIBS analysis, unlike the wet chemical analyses which are limited to a single element. LIBS was used for determination of trace elements, such as chloride and sulfur, in cement based materials [7, 8]. It can be considered as a meso-scale technique, with spatial resolution in *mm* range. Because chloride ions are present only in the cement paste and not in the aggregate particles, it is important that LIBS can discriminate between these locations based on other elements, such as *Ca* (only present in the cement paste phase) and *Si* (only present in the aggregates).

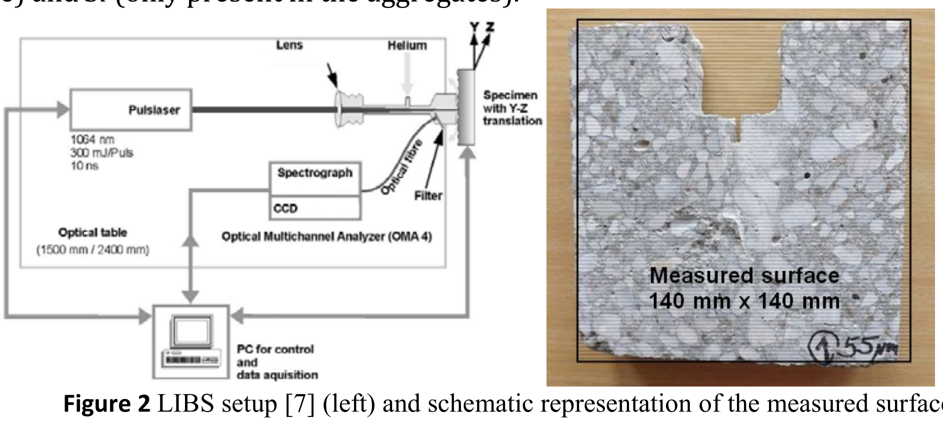


Figure 2 LIBS setup [7] (left) and schematic representation of the measured surface (right)

In this work, LIBS was used to determine two dimensional chlorine, sodium, and calcium distribution in cracked concrete specimens exposed to chloride ingress. After the chloride exposure, three specimens were dry cut and the element distributions were determined by LIBS. An area of 140x140 mm was scanned with a spatial resolution of 1 mm.

3 Results

3.1 Cracking results

In total, analyses of three specimens are shown here. In order to control the obtained crack width, LVDTs are placed on both sides of the specimen at the bottom of the notch, where the crack is expected to initiate. Their average is used as a feed-back signal for the machine, and controls the whole loading process. In this way, a stable cracking procedure is performed.

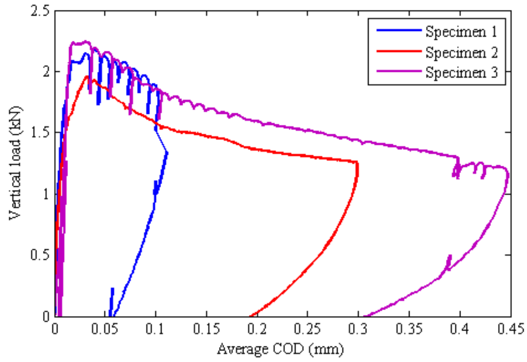


Figure 3 Load-COD curves of the tested specimens

As shown in figure 3, specimens are first loaded until a certain average COD (crack opening displacement) is achieved, and then unloaded, and their final crack width is recorded. The unloaded crack width is somewhat smaller than the maximal crack width achieved during the cracking procedure, i.e. prior to unloading (figure 3). For specimens used in this study, the surface crack widths were: 0.055 mm for specimen 1, 0.190 mm for specimen 2, and 0.305 mm for specimen 3.

In the standard wedge-splitting test, a crack initiates in the notch, and becomes deeper and wider as the load increase. In the modified test as used herein, the crack branches horizontally as it reaches the steel reinforcement (see an example in Figure 4). The wider the surface crack is, the more debonding at the steel/concrete interface occurs, similar to that occurring in a reinforced concrete beam [4]. This makes the proposed geometry suitable for studying chloride ingress and reinforcement corrosion in cracked concrete, while taking into account the importance of cracking along the steel/concrete interface.

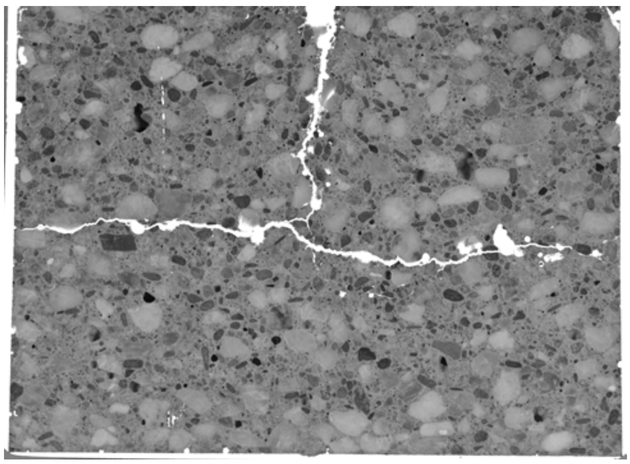
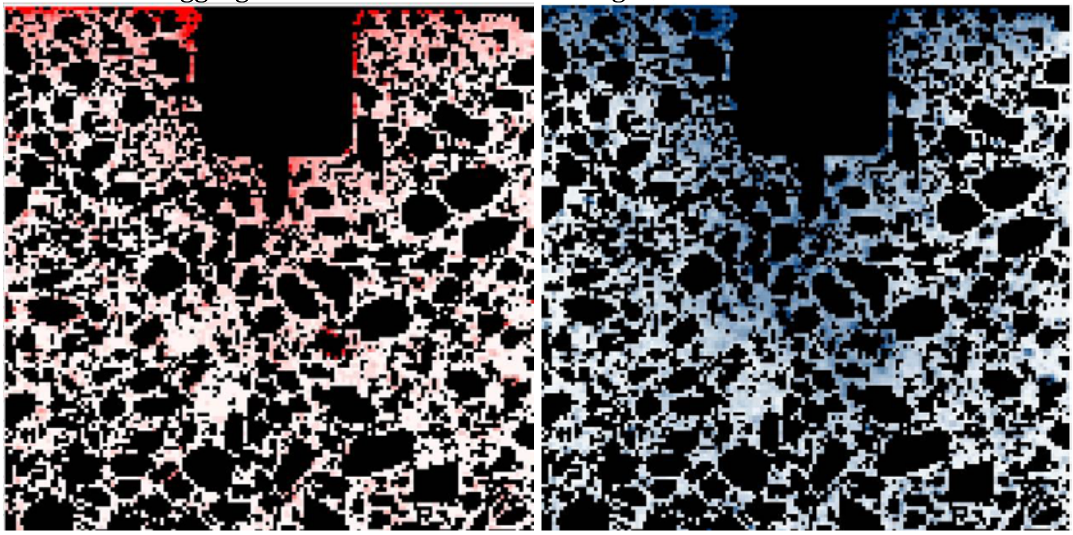


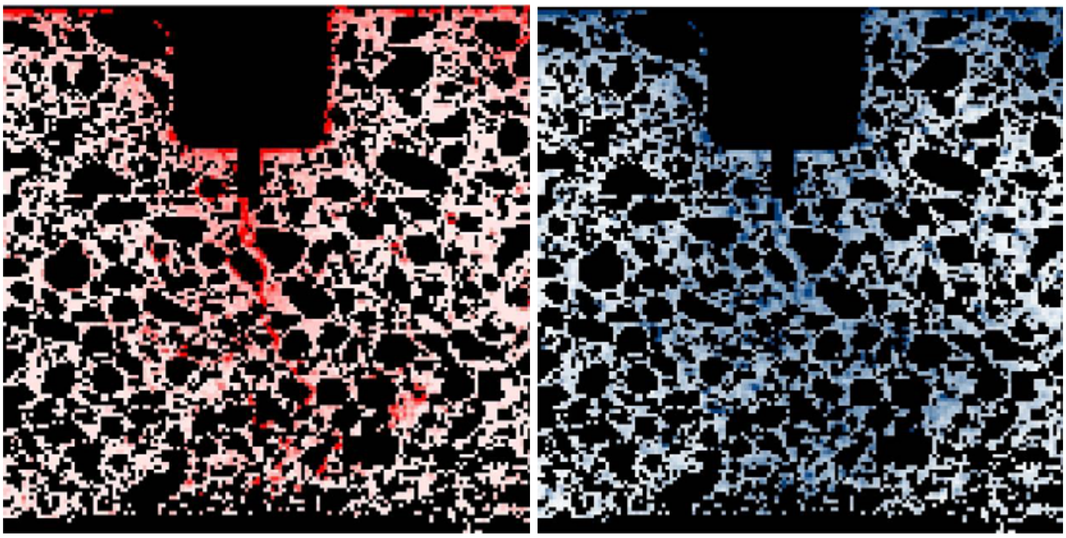
Figure 4 Impregnated crack of a MWST specimen from a related study under ultraviolet light [9]

3.2 Chloride and sodium profiles

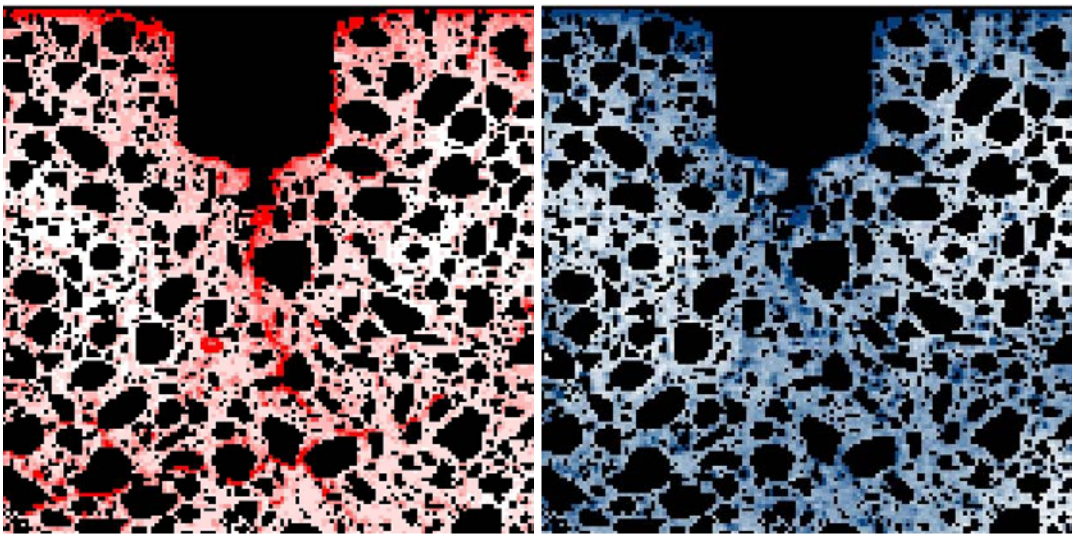
Due to the space limitations, only chloride and sodium profiles for three tested specimens are shown here. Coarse aggregates are left out from the images, and shown in black.



(a) Specimen 1 (w_{cr}=0.055 mm)



(b) Specimen 2 (w_{cr}=0.190 mm)



(c) Specimen 3 (w_{cr}=0.305 mm)

Figure 5 Distributions of chlorine (left) and sodium (right) for the testes specimens. Brighter colors indicate high concentration.

4 Discussion

From the LIBS measurements, it is possible to see that concrete cracking has a marked influence on ingress of chloride and sodium. Penetration initiates from the recess, where the NaCl solution was poured, but also from the top of the specimen, where the solution was poured. In specimen 1, which has the smallest crack width (0.055 mm), chloride penetration depth around the notch is similar to that around the rest of the recess. This indicates that the influence of cracking is insignificant. A pronounced influence of cracking is visible in specimens 2 and 3, however. In specimen 2, horizontal chloride penetration around the crack is observed. Furthermore, as the crack branches horizontally (i.e. parallel to the reinforcing steel), the chloride ions penetrate trough the interface and to the surrounding concrete. This is even more pronounced in specimen 3. Although no quantitative assessment is performed herein, it is observable that the chloride penetration from the horizontal crack into the concrete in specimen 3 is comparable to the chloride penetration from the surface. This is in line with findings of Win et al. [10]. It is also in accordance with observations of Pease [4], who found that cracking at the steel/concrete interface is an important factor with respect to chloride ingress and subsequent reinforcement corrosion. Also, cracking in concrete tends to occur within the mortar phase and the ITZ, and around the coarse aggregates. Similarly, chloride ions penetrate through the mortar and the ITZ and around the aggregate. For modelling of chloride ingress (especially in cracked state) it is important therefore to treat concrete as a heterogeneous material, i.e. to use meso-scale models [11].

When sodium profiles are concerned, a similar trend is observed. However, the ingress of sodium is already increased around the small crack (0.055 mm) in specimen 1. This is even more pronounced in specimens 2 and 3. This indicates that ingress of sodium ions is somewhat more sensitive to existence of small cracks (such as in specimen 1) compared to chloride ions. Also, the local increase in sodium concentration close to the exposed surfaces and cracks indicates higher penetration depth compared to chloride. This is probably due chloride binding. As a consequence, chloride penetration depth cannot be indirectly estimated by measuring sodium profiles, which is easier for many measurement methods.

5 Conclusions

In current work, the influence of cracking on ingress of chloride ions into concrete is discussed. A method for specimen preparation and cracking based on the wedge splitting test is proposed. Specimens were exposed to wetting and drying cycles with NaCl solution for a prolonged time period. In the end, element distributions of sodium and chlorine were determined by LIBS. Based on the findings, the following conclusions can be drawn:

- The proposed cracking method and specimen design enable creating bending-type cracks, with debonding occurring at the steel/concrete interface. This is similar to the behaviour of reinforced concrete beams.
- LIBS can be used as a reliable tool for two-dimensional elemental mapping on the meso-scale. Multiple elements can be measured in the same analysis, which is an advantage over wet chemical techniques.
- Chloride ingress is affected by the cracking. The wider the surface crack, the more chloride penetration occurs. In wide cracks, penetration of chloride ions parallel to the steel occurs, due to the damage in the steel/concrete interface.
- Penetration depth of sodium is higher than that of chloride, also around the cracks.

Further results of the study will provide insights on the influence of cracking on chloride ingress. Combined with findings of a related study on corrosion in cracked concrete [12], the influence of cracks on service life and long term durability of reinforced concrete structures will be assessed.

5.1 Acknowledgements

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