µ-XRF – CHARACTERISATION OF CHLORIDE INGRESS AND SELF-HEALING IN CRACKED CONCRETE

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ABSTRACT
In this paper we illustrate the applicability of µ-XRF for investigations of chloride ingress and self-healing in cracked concrete. A cracked and an uncracked concrete core exposed to seawater for more than 30 years were investigated with µ-XRF. The cracked sample had higher chloride ingress in the outer part of the concrete core (first 20 mm). Parts of the investigated crack were self-healed with calcium and magnesium rich phases. It was concluded that µ-XRF is a powerful tool for fast and detailed characterization of elemental distribution; e.g. chloride ingress, as it is able to detect spatial irregularities caused by for example cracks.

Key words: Cracking, Chlorides

1 INTRODUCTION
As part of the Norwegian Public Road Authorities (NPRA) Ferry-free coastal road E39 project, NTNU is collecting long term data from field exposed reinforced concrete structures on chloride ingress and the extent of corrosion in the vicinity of cracks.

There is agreement in literature that cracks in concrete increase the ingress of harmful species like chloride ions [1]. However, it is also expected that in the long term effects like self-healing of cracks may reduce the later chloride ingress [1, 2]. In case of a self-healed crack the chloride ingress depends on the resistance to ingress of the "healing" phase. The most commonly used technique to analyse chloride ingress in concrete is profile grinding of extracted cores and subsequent chemical analysis for chlorides [3]. However, this method is destructive and time consuming. Furthermore, the collected powder is homogenized over the entire area; thus, the potential impact of cracks on ingress will be unclear. 2D characterization of chloride ingress might be obtained by spraying the surface with $AgNO_3$, which reacts with available chlorides.

The method was for example used by Michel et al. (2013) to illustrate the ingress through primary cracks and debonding between concrete and reinforcement [4]. The disadvantage of the method is that only the depth of penetration of a given threshold is determined. SEM and µ-XRF (µ-X-ray fluorescence) and other chemical imaging techniques, on the other hand, can provide equivalent or better information to profile grinding and in 2D [5]. Similar to bulk XRF, µ-XRF uses X-ray excitation to induce characteristic X-ray fluorescence emission from the sample for elemental analysis. Compared to other chemical imaging techniques, µ-XRF has two major advantages. µ-XRF is less sensitive to surface roughness and there is no or only little sample preparation required [5]. Furthermore, big samples up to 20 x 15 cm with a weight up to 5 kg can be measured. Thus, µ-XRF can fast deliver results on large concrete samples. Besides chloride mapping other elements can be investigated and local abnormalities like cracks or other forms of chemical attack can be detected additionally [5].

The objective of this study is to illustrate the applicability of µ-XRF for characterization of chloride ingress and self-healing of cracks in concrete.

2 MATERIALS AND METHODS

A cracked and an uncracked concrete core exposed to seawater for more than 30 years were investigated. The cores had a length of 200 mm and a diameter of 100 mm. The cracks in the cracked concrete were measured with a crack-width ruler. The crack width varied unsystematically between 0.3-0.7 mm. The crack was perpendicular to the exposed surface and oriented transverse to the main reinforcement and parallel to the stirrups. The cores were cut perpendicularly to the surface with a water-cooled concrete saw in two halves. One half of each core was sprayed with a 0.1 M $AgNO_3$ solution and the chloride ingress was measured with a slide gauge according to [6].

The other halves were without further preparation investigated with a M4 Tornado µ-XRF apparatus from Bruker. The instrument uses a silicon drift detector energy dispersive spectrometer (SDD-EDS). The µ-XRF is equipped with a silver X-ray tube and polycapillary lenses focusing the X-ray beam to a spot size of 25µm. For point analysis, a current of 200 µA and a voltage of 50 kV were used. For line scans and elemental mapping the current was increased to 600 µA. The chamber pressure was 20 mbar at all times. The elemental mapping area was 150 x 50 mm.

Preliminary results on the chloride ingress in a cracked (CC) and an uncracked concrete (UC) core and self-healing of cracks are presented.

3 RESULTS AND DISCUSSION

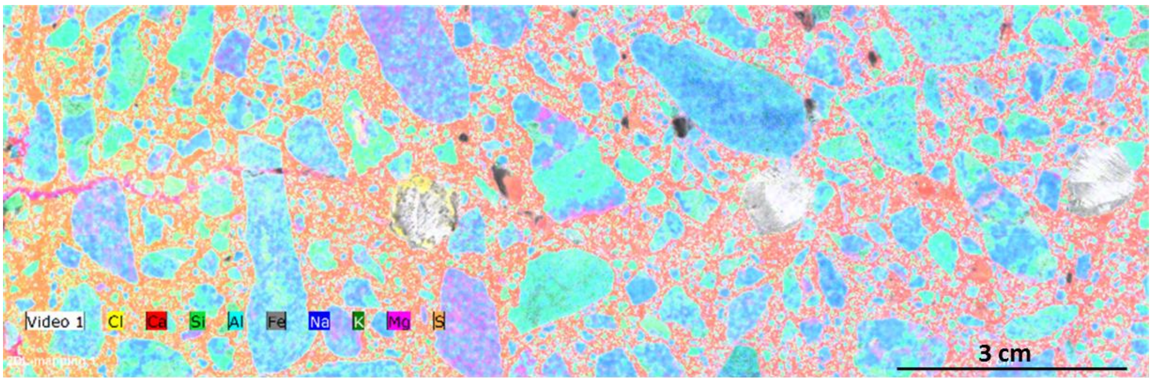

Figure 1: Elemental mapping of cracked concrete core (CC)

Figure 1 shows an elemental map of the cracked concrete core including Cl, Ca, Si, Al, Fe, Na, K, Mg and S. No sample preparation was required and the data acquisition took 2.5 h.

Chloride maps of the cracked and the uncracked concrete cores are shown in Figure 2. In the maps, the chloride ingress depth measured with $AgNO_3$ is indicated with the light grey area.

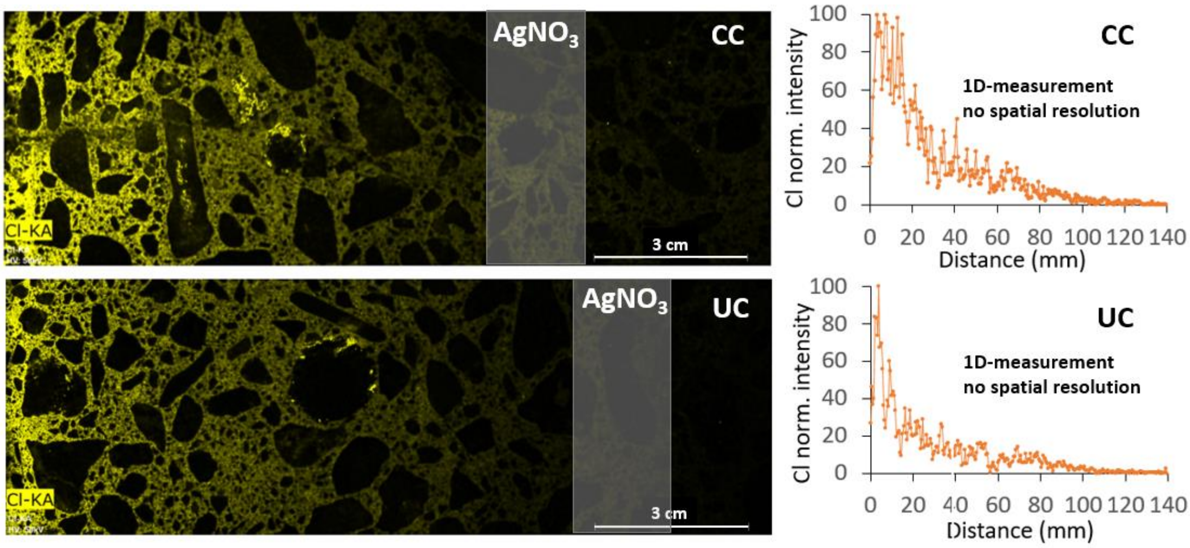

Figure 2: Qualitative 2D-chloride map of cracked ('CC', above) and uncracked concrete cores ('UC', below), as well as normalized intensity of chloride line scans from the surface to the bulk of the cores (average of six line scans)

Next to the chloride maps in Figure 2, the measured normalized intensity of chloride as a function of the depth from the surface is shown. The results show an average of six line scans, each with 250 measuring points.

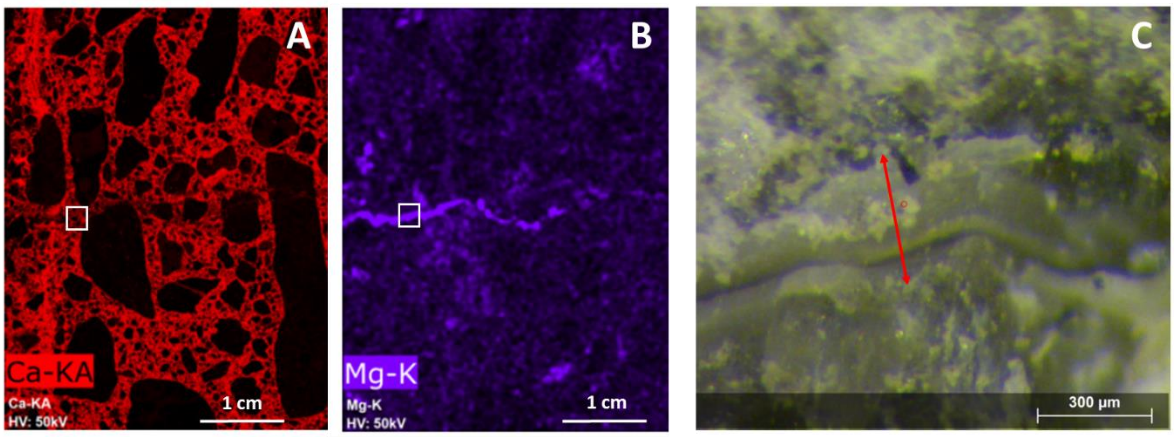

Figure 3: Calcium (A) and magnesium (B) map and close up picture (C) on self-healed crack in cracked core (red line indicating original crack width)

µ-XRF showed that the cracked core has higher chloride levels in the outer 20 mm. However, the total depth of chloride penetration is comparable in the cracked and uncracked concrete. By spraying with silver nitrate the detected chloride penetration was slightly lower in the cracked concrete compared to the uncracked concrete (Figure 2). The reason for this is at present unknown.

Figure 3 shows calcium and magnesium maps in addition to a close up picture of a self-healed crack in the cracked core (CC). It appears that precipitated solids almost close the crack. The red arrow in Figure 3C is marking the original crack width of about 0.4 mm in the shown area. Similar areas were found all over the sample where the crack was almost completely healed. Point analysis was performed on the phases precipitated in the crack. The results showed that the phases are rich in calcium and magnesium with a ratio of about 1/1, indicating the potential presence of e.g. dolomite.

In other areas the crack appeared open or was filled with debris potentially from the cutting of the cores. Self-healing of the crack can explain why the total depth of chloride penetration was comparable in the cracked and uncracked cores, even with a crack width of up to 0.7 mm in some parts.

4 PERSPECTIVES

µ-XRF is shown to be a powerful tool for fast elemental analysis (e.g. chloride ingress) of large concrete samples with little effort. With a spatial resolution of 25 µm it is in addition feasible for detailed analysis of areas of specific interest. In this investigation self-healing of a crack was characterized.

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