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## Using micro X-ray fluorescence to image chloride profiles in concrete

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## ABSTRACT

Corrosion of steel reinforcement in concrete is not easy to detect until cracking has initiated. When there is a question about Cl intrusion into concrete, cores are taken, the sample is ground in controlled thicknesses, and then the powder is analyzed by titration. This paper uses micro X-ray fluorescence (μXRF), a non-destructive chemical imaging technique, to obtain equivalent or better information than profile grinding methods with less human involvement. Fifteen different comparisons are made between profile grinding and μXRF from the same concrete and the results are comparable. Examples are also presented where the spatial measurements made by μXRF provide insights that are not possible with the conventional profile grinding method. This means the Cl profile can be obtained with μXRF with less human effort while providing additional insights not possible with the typical profile grinding analysis.

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## 1. Introduction

The most prevalent and costly durability problem with structural concrete is the corrosion of internal reinforcing steel from Cl ions [1–5]. According to the Federal Highway Administration (FHWA), corrosion causes \$8.3 billion in damage annually to the transportation infrastructure [1]. The Cl ions are typically contributed by deicing salts, ocean water, or from clays rich in ionic salts [6–7]. While these materials are sometimes found within materials used to make concrete, typically they penetrate the concrete from an external surface.

The most widely used method to investigate Cl ingress into concrete is to destructively take cores, powder the concrete at controlled depths, and then analyze the powder with titration for Cl concentration. A version of this technique is used in many standards, including ASTM C1152, AASHTO T 260-97 and NT Build 208. These measurements provide insight into the rate of Cl ingress and can be used to evaluate the quality of concrete, the amount of Cl present, and to project the long term service life of the structure.

These techniques require that at least 10 g be collected from a number of different depths of the concrete. This can be time consuming. The collected powder is a combination of both aggregate and cement paste. Since the Cl is primarily contained in the paste, the aggregate dilute the sample. It would be possible to reduce the amount of material and time

needed to complete the test if it was possible to focus the examination of chlorides within the paste.

One solution to this problem would be to use imaging techniques capable of mapping chemistry and discern between the aggregate and the paste with minimal human intervention. This technique could also identify local abnormalities that will alter the results like cracks, Cl rich aggregates, or other forms of chemical attack like alkali silica reaction, sulfate attack, or carbonation. The current profile grinding technique only investigates the average Cl concentration and so cannot provide insight into any of these phenomena.

Several chemical imaging techniques have been used to investigate Cl penetration in concrete and paste. Jensen et al. [8], and Mori et al. [9], used electron probe microanalysis (EPMA) to measure Cl concentration profiles in cement paste and concrete samples. In addition, Dempere et al. [10], used both scanning electron microscopy with electron dispersive spectrometer (SEM-EDS) and EPMA techniques to map Cl content in concrete. These studies all used electrons to interrogate the surface of the sample. The results also showed that the Cl concentration was consistently overestimated when compared with results from profile grinding. Another important conclusion was that the results from SEM-EDS and EPMA are dependent on the sample preparation [8–10]. For all of these reasons, electron based imaging methods are not widely used to evaluate Cl concentration in concrete or paste.

This work uses a non-destructive micro-analysis technique called micro X-ray fluorescence (μXRF) to image a cross section of concrete and determine the Cl concentrations. This technique is similar to bulk X-ray fluorescence (XRF), but uses a polycapillary optic to focus X-

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rays to a size of approximately 50  $\mu\text{m}$  in diameter, whereas bulk XRF investigates the sample with a 1 cm diameter spot.

$\mu\text{XRF}$  has many advantages over electron based imaging techniques such as SEM – EDS or EPMA with their typical configurations [11–14]. X-rays interact more weakly with matter than electrons and so they penetrate deeper into the sample (up to 1 mm for X-rays compared to a few microns for electrons) [15–16]. This deeper penetration makes the results less sensitive to the surface roughness. Furthermore,  $\mu\text{XRF}$  does not require conductive coatings to reduce electron build up or charging [8–11,17].

A previous publication has used  $\mu\text{XRF}$  to investigate the Cl profiles within mortar [18]. This work used individual points at different depths to determine Cl content but they did not compare their measurements to profile grinding at comparable times. This work makes fifteen different comparisons between  $\mu\text{XRF}$  and profile grinding, and examples are given where spatial measurements made by  $\mu\text{XRF}$  provide insights that are not possible with profile grinding.

## 2. Experimental methods

### 2.1. Materials and mixtures

Six different concrete mixtures were investigated in this work. The mixtures have a water-to-cementitious ratio (w/cm) of 0.45. Four ASTM C618 Class C and one Class F fly ashes are used as 20% of the mass of the binder. One mixture used only portland cement as the binder. The cement is an ASTM C150; Type I. The chemical composition of cementitious materials is in Table 1 and was obtained by bulk XRF. The coarse aggregate is a dolomitic limestone and the fine aggregate is a locally available natural sand.

### 2.2. Mixture proportion and sample preparation

The concrete mixtures were prepared according to ASTM C192. All of the aggregate, both coarse and fine, were brought into the temperature controlled mixing facility at least a day before and their batch weights were corrected based on their moisture content. The aggregates were charged into the mixer along with approximately two-thirds of the mixing water. The combination was mixed for 3 min. Next, the walls of the mixer were scraped to remove material that stuck to the walls. Then the cement and fly ash was loaded into the mixer, followed by the remaining mixing water. The mixer was turned on for 3 min. Once this mixing period was complete, the mixture was left to “rest” for 2 min while buildup of material along the walls was removed. Next the mixer was run for 3 min. The slump, unit weight, and the air content

were measured according to ASTM C143, ASTM C138, and ASTM C231, respectively. The concrete mixture proportions and fresh properties are given in Table 2.

The concrete was placed in 12  $\times$  12  $\times$  8 cm plastic molds. The samples were cured for seven days at 23  $^{\circ}\text{C}$  with a lid. Next the sample was stored in a saturated lime solution for seven days to minimize mass transport other than concentration driven diffusion. Next, the area between the concrete and the container was sealed with silicone and the specimen was then placed in 165 g/L aqueous sodium chloride solution according to ASTM C1556 for either 45, 90, or 135 days at 23  $^{\circ}\text{C}$ . Next, the Cl solution was removed and the samples were stored for 24 h in laboratory conditions. Then, the sample was powdered at 1–5, 5–10, 10–15, and 15–20 mm depths parallel to the exposed surface using a drill press with 25 mm core bit. These depths were different than those recommended by ASTM C1556. The profile had a length of approximately 7.5 cm across the surface of the sample to obtain 15 g powder for each investigated layer. Finally, the powder was analyzed for acid-soluble Cl content with silver nitrate according with ASTM C1152.

After the powder was collected, the remaining sample was split and the exposed cross section was polished on a sanding belt for 15 min with 120 grit sandpaper to create a flat surface. Ethanol was then used to remove dirt and residue from the polished surface. This flat surface allowed for easier interpretation of the  $\mu\text{XRF}$  and optical microscopy results.

In addition, two concrete cores were taken from local in-service bridges that were 10 cm diameter and 15 cm height. These samples were polished with the same procedure and then analyzed with  $\mu\text{XRF}$ . There were no historical records available providing specific information on concrete mix design of the field samples.

### 2.3. $\mu\text{XRF}$ test procedure

The  $\mu\text{XRF}$  analysis was conducted using the Orbis by EDAX. The instrument uses an 80 mm<sup>2</sup> Silicon Drift Detector Energy Dispersive Spectrometer (SDD-EDS) and a capillary optic that produces a 50  $\mu\text{m}$  diameter beam. Images are created by moving the sample under the stationary X-ray beam. The X-ray beam causes characteristic fluorescence X-rays to be emitted at each spot, the intensity of these characteristic X-rays is measured by the SDD-EDS and stored in a database for later processing and analysis. This analysis is able to detect elements at 0.1% by weight [19]. A laser control system with a fixed focal length was used as a secondary focusing tool to ensure a consistent geometry between the X-ray source, sample, and detector. This system is used to adjust the height of the sample such that the sample is in optimal focus.

Table 3 summarizes the settings used by the  $\mu\text{XRF}$  in this work. More details can be found in other publications [14]. An overall count rate of 20,000 counts per second was obtained with a 400 ms dwell time per pixel by using an accelerating voltage of 40 keV, a probe current of 1 mA, and a detector dead time near 20% as suggested by Janssens [19]. Each automated scan was  $\approx$  20 h per sample. This time can be reduced with future refinements to the method.

The  $\mu\text{XRF}$  uses a rhodium X-ray tube to produce polychromatic X-rays. The rhodium  $\text{L}\alpha$  line overlaps with the chlorine  $\text{K}\alpha$  line, complicating compositional analysis. Because of this a 25  $\mu\text{m}$  thick Al filter was used to remove the low energy rhodium radiation. All scans were conducted under a 1.35 Torr vacuum to reduce the absorption of X-ray emission by  $\text{N}_2$ ,  $\text{O}_2$  and Ar gas [19–20].

The raw data from  $\mu\text{XRF}$  is the number of fluoresced X-rays in a certain energy window which includes background radiation as well. To determine concentration information, a set of reference standards were used to develop a calibration curve to change the count data to Cl concentration. This was done by making concrete samples with w/cm of 0.45 with known amounts of NaCl. A similar concrete mix design as the mixture with no fly ash was used to make the reference samples.

**Table 1**  
Chemical composition with bulk XRF (% weight).

Oxide	Cement (PC)	FA-C1	FA-C2	FA-C3	FA-C4	FA-F
SiO <sub>2</sub>	20.40	39.13	36.21	38.34	38.13	56.72
Al <sub>2</sub> O <sub>3</sub>	5.03	20.37	19.94	19.87	20.99	20.29
Fe <sub>2</sub> O <sub>3</sub>	2.95	6.15	6.67	6.12	5.46	5.62
CaO	62.89	21.18	23.96	23.07	15.54	9.95
MgO	2.08	5.33	5.17	5.16	3.71	2.97
Na <sub>2</sub> O	0.35	1.60	1.67	1.53	7.88	0.54
K <sub>2</sub> O	0.35	0.65	0.52	0.62	0.77	1.38
TiO <sub>2</sub>	0.28	1.33	1.44	1.43	1.31	1.12
MnO <sub>2</sub>	0.10	0.02	0.03	0.02	0.04	0.09
P <sub>2</sub> O <sub>5</sub>	0.16	1.60	1.44	1.09	0.67	0.13
SrO	0.16	0.34	0.38	0.35	0.72	0.27
BaO	0.12	0.72	0.69	0.64	1.47	0.26
SO <sub>3</sub>	3.05	1.37	1.44	1.14	2.90	0.51
L.O.I	2.09	0.24	0.15	0.62	0.41	0.16
Moisture	0.16	0.11	0.04	0.01	0.03	0.02

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