An Innovative Approach for Measuring Chloride Threshold Levels in Reinforced Concrete

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ABSTRACT: Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful analytical technique that has been used successfully in many fields such as geology, biology and materials sciences but has very limited application in concrete technology. Its main advantage is the possibility to spatially identify and quantify trace elements in solid samples at a micro or meso-scale level. This paper presents the potential application of LA-ICP-MS for the measurement of the critical chloride level ($C_{cr}$) leading to the depassivation of steel at the concrete-steel interface. In the paper, the state-of-the-art regarding the determination of $C_{cr}$ is reviewed and preliminary experimental work concerning the instrument calibration and detection limit is presented. Using cement pastes and finely ground pressed concrete with different chloride content, the influence of different operating conditions was studied in order to optimize the method’s sensitivity. Calcium was determined as an indicator of cement content. Within a resolution range smaller than 300 µm, correlation coefficients of over 0.94 between the chloride to calcium signal intensity ratio and the chloride content were obtained. The results showed that it is possible to use this technique for the intended purpose. Further improvements regarding reproducibility of the method are under development.

1 INTRODUCTION

1.1 Chloride Threshold Values

The measurement of chloride threshold values is a very complex topic. Firstly, it involves a large number of factors such as concrete and pore solution compositions [1,2], steel type and surface characteristics [3,4] and exposure environments [5]. Secondly, and probably most importantly, there is lack of agreement in its definition, compliance methodologies and consequently reporting options.

The determination of the chloride threshold value relies on the sensitivity of the depassivation detection technique used since no direct measurement is available. Depassivation of steel can be assessed by monitoring different parameters such as the electrochemical potential, the corrosion rate, the macrocell current and the concrete resistivity. These are often complemented by auxiliary measurements of temperature, relative humidity and oxygen transport. The critical chloride content is then usually expressed as the chloride content determined at the time when a sudden change in the monitored parameter is observed.

Another difficulty regarding the determination of the chloride threshold value arises from the fact that no uniform system for specifying the chloride content in concrete has been established. Several adopted forms are used: total chloride content by weight of concrete, cement or binder; water soluble (or free) chloride content by weight of concrete, cement or binder and chloride concentration to hydroxide concentration ratio [6]. Because in hardened concrete the quantity of cement or binder is often difficult to determine, the total chloride content by weight of concrete seems to be the most adequate reporting option.
Over the last years a great amount of research has been carried in order to more accurately detect depassivation. However, little focus has been put in concrete sampling for chloride determination and this is probably one of the main reasons for the large variation in the reported threshold values. Essentially, samples are ground off as close as possible to the steel and later analyzed by means of Volhard titration, potentiometric titration or X-Ray diffraction fluorescence. Because the concrete is removed by mechanical means, the analysed material is only representative of the bulk concrete around the reinforcement and the reported value represents an average chloride content, as can be seen in [7,8] where 25-30 mm layers where ground. However, as shown in [9] this chloride content can differ from that at the steel interface contact layer and therefore, the real chloride content at the pit remains uncertain.

1.2 LA-ICP-MS

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful analytical technique for the characterization of solid samples in materials science. It enables multi-element spatial identification and quantification at very low concentration levels and at a micro or meso-scale.

In laser ablation (LA), a laser beam is focused on the surface of a solid sample, ablating the material and partially vaporizing it, creating a solid aerosol. This plume is then transported by an inert gas (argon or helium) into the plasma (ICP) where the elements are atomized and ionized. Finally the ions are selectively detected by the mass spectrometer (MS) [10]. Figure 1 schematically represents LA-ICP-MS technique.

![Figure 1: LA-ICP-MS technique](image)

As stated in [12], there is no limitation to the type of sample which may be ablated. A wide range of applications in different fields has been presented in [13]. These include: environmental monitoring (tree barks, sea shells, corals and airborne particulates); geology and geochronology; archaeology; waste sample analysis and forensic studies (fingerprinting and teeth analysis).

In concrete technology, LA-ICP-MS has been only applied in few studies, such as alkali silica reaction mechanism [14] and radioactive isotopes analysis [15]. To our knowledge, very limited research regarding the evaluation of chloride profiles in concrete has been done using this technique. Since this technique has a resolution range of less than 300 µm, it is suitable to detect concentration changes at a meso-scale. Therefore, the aim of this paper is to investigate the critical conditions for depassivation of steel, by assessing the chloride profiles along the steel-concrete interface and establish relationships between concrete’s macro and meso or microstructure.
2 EXPERIMENTAL

2.1 Materials

In this study, cement pastes, concrete powder and depassivated reinforced concrete samples were used.

Cement pastes (made from Skövde Standard Portland cement) containing 0.05%, 0.1%, 0.5% and 1% chloride per weight of cement were prepared by dissolving NaCl in deionised mixing water. The water/cement ratio used was 0.4. Disk specimens with a diameter of 40 mm were cast and cured at 40 °C during 3 days. In order to prevent water evaporation, the specimens were sealed in plastic bags. After curing, the specimens were sawn to a thickness of 10-15 mm and the surface was slightly polished using 180 grit paper.

Concrete powders containing known chloride content (see Table 1) were provided by SP Technical Research Institute of Sweden, where the chloride content in the concrete is determined by potentiometric titration in accordance with AASHTO T260 [16]. The powders were poured into a stainless steel sample holders (5 mm in diameter and 10 mm in height) and compressed to 500 MPa to form a “solid surface” for ablation.

A depassivated reinforced concrete specimen was also analysed. Materials and procedure for the fabrication and testing of this specimen is provided by CBI Swedish Cement and Concrete Research Institute [17]. After depassivation detection, the specimens were sawn in order to enable rebar removal with minimum interference in the steel-concrete interface. No surface treatment whatsoever was performed along the scanned area.

Table 1: Total chloride content in the reference concrete powders used (% by mass of concrete).

<table>
<thead>
<tr>
<th>Reference 1</th>
<th>Reference 2</th>
<th>Reference 3</th>
<th>Reference 4</th>
<th>Reference 5</th>
<th>Reference 6</th>
</tr>
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<tr>
<td>0.024</td>
<td>0.070</td>
<td>0.118</td>
<td>0.198</td>
<td>0.254</td>
<td>0.314</td>
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<tr>
<td>± 0.002</td>
<td>± 0.005</td>
<td>± 0.012</td>
<td>± 0.008</td>
<td>± 0.005</td>
<td>± 0.015</td>
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2.2 Instrumentation

A CETAC LSX-200 Laser Ablation System coupled to a quadrupole ICP Mass Spectrometer (ELAN 6000 from Perkin Elmer) was used for the analysis. The experimental parameters of both systems are described in Table 2. Experimental parameters were optimized in order to obtain maximum ion intensity of the analyte (chloride).

In most of the concrete samples it is difficult to assess the cement content. To overcome this limitation, calcium was also measured and the chloride signal intensity is divided by the calcium signal intensity. The normalised resulting signal ratio is the measured parameter that is plotted against the total chloride content in the reference samples for the calibration purposes. This procedure is, in LA-ICP-MS, referred to as internal standardization.

Table 2: Instrument operating conditions and experimental parameters of the LA-ICP-MS.

<table>
<thead>
<tr>
<th>ELAN 6000 ICP-MS</th>
<th>CETAC LSX-200</th>
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<tbody>
<tr>
<td>RF Power (W)</td>
<td>1300</td>
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<tr>
<td>Dwell Time (ms)</td>
<td>50</td>
</tr>
<tr>
<td>Sweeps</td>
<td>6</td>
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<tr>
<td>Carrier Ar gas flow rate (l/min)</td>
<td>0.77 – 1.0</td>
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3 RESULTS AND DISCUSSION

3.1 Cement Pastes and Reference Concrete Powder

A typical LA-ICP-MS profile is shown in Figure 2. The instrument parameters used are described in Table 2 (see Experimental section) and in the figure. The start of the ablation process
is marked by a sharp increase in the analyte signal while the end can be observed in the form of a “tail”. With the laser off, data is acquired for an initial period in order to retrieve the basic lines.

From Figure 2 it can be seen that both calcium and chloride present relatively stable signals during the whole ablation process, indicating a uniform distribution of these elements along the surface. However, because of the high sensitivity of this technique, minor irregularities in the sample surface can generate fluctuations in the detected signal, regardless of the fact that surfaces were polished.

In order to obtain the calibration curves (Figures 3 and 4), the individual chloride signals were divided by the calcium signals and the average chloride-to-calcium signal ratio was plotted against the known chloride content. In both cases high correlation coefficients were obtained indicating that this methodology can be used for the intended purpose. Still, differences between the two correlations were observed. Here the calcium content seems to be the most influencing factor. When comparing the calcium signals obtained for cement pastes and concrete powder, this is about one order of magnitude higher in the first case, thus explaining the lower value for the slope in the cement paste calibration curve.

3.2 Concrete Specimen

Two main regions were analyzed within the concrete-steel interface presented in the experimental section. Figures 5 and 6 present the scanned positions and their respective chloride profiles obtained based on the calibration curve presented above in Figure 4. As expected, higher chloride contents around the pitting positions were determined. This can be seen in Figure 5 but also between the Cl profiles #5 and #7 in Figure 6. A common characteristic is the clear existence of air voids around these positions, facilitating the chloride penetration to the concrete-steel interface.

Naturally different chloride contents were found between the two analyzed positions. These may be attributed, for instance, to differences in the steel surface at the time of casting. For the
specimen shown, the chloride profiles drawn in [17] indicate that at the depth of the reinforcement, the total chloride content, measured by means of potentiometric titration (macro-scale level), is in the range of 0.2-0.3 wt.% of concrete. It can be seen that the chloride profiles along the reinforcement, obtained by means of LA-ICP-MS technique, are in the same order of magnitude (0.1-0.4 wt.% of concrete), providing a good indication on the possibility for the application of this technique.

Figure 3: Calibration curve for cement pastes.

Figure 4: Calibration curve for concrete powder.
This preliminary study indicates the possibility of using LA-ICP-MS for the determination of the chloride threshold values. This can be seen from the high calibration correlations resulting in comparable total chloride contents obtained by different means (potentiometric titration and LA-ICP-MS). The main advantage of the presented technique is that within a less consuming time frame, it enables the chloride profile study along the whole concrete-steel interface (spatial distribution) including the pitting positions and at a scale that cannot be achieved by conventional techniques such as powder titration. Because LA-ICP-MS is a semi-destructive method the same sample can be analyzed later for microstructure by other means such as LV-SEM-EDS. Correlations between the chlorides distribution, material properties (porosity, alkalinity, cement content, steel composition) and exposure environments (temperature, moisture, oxygen) can be obtained in order to describe the conditions through which the pitting corrosion occurs. Due to the number of influencing variables, further developments regarding the optimization of the control parameters are in progress in order to ensure high repeatability and reproducibility.
5 PREFERENCES