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## Review

# Non-destructive measurement of chloride ions concentration in concrete – A comparative analysis of limitations and prospects

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## HIGHLIGHTS

- Measuring chloride is crucial for service life assessment of concrete structures.
- Measurement techniques mainly based on electrochemistry and electromagnetics.
- Based on the level of assessment different techniques have pro and cons.
- For existing structure assessment varies from visual to detailed lab investigation.
- Electrochemical sensor are suitable for installation in new structures.

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## ABSTRACT

In this work, the different techniques for non-destructive in situ measurement of chloride ion concentration are presented. Non-destructive (ND) in situ measurement is crucial for reliable and continuous determination of chloride ion concentration in concrete. Over the last 20 years, several studies have been performed on ND measurements. These were mainly focused on the application of electrochemical and electromagnetic techniques. Each technique has its advantages and disadvantages. Depending on the requirement of assets managers and constructors and considering the limitations, these techniques can be well applied. The main concepts and comparative analysis, in view of possibilities and limitations, of these non-destructive techniques are presented in this paper.

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## 1. Introduction

### 1.1. Chloride based reinforcement steel corrosion

The concentration of chloride ions is one of the most important indicators for the deterioration of reinforced concrete (RC) structures [1–6]. In the presence of a critical amount of chloride ions, also known as critical chloride content, the reinforcing steel undergoes rapid localized corrosion. Such localized corrosion can form “pits”, giving rise to the term localized corrosion [7–9]. Although localized corrosion might not have a significant immediate consequence for the daily operation of a reinforced concrete structure, it may affect the structural performance of the concrete structure in the long term and under specific load or environmental conditions, such as earthquakes [10,11]. Corrosion drastically reduces the tensile strength of steel, and thus compromises the load bearing capacity of reinforced concrete. During corrosion, the passive film of iron oxide, initially formed on the surface of steel and inhibiting further corrosion, is destroyed. In case of chloride induced corrosion, this passive film is locally broken. The on-going corrosion process results in the formation of voluminous corrosion products. This results in early crack formation, propagation and possible detachment of the concrete cover. Structures near marine environment or those exposed to de-icing salts are prone to pitting corrosion. Specially, the splash zone near seawater, which is the area near the air/water interface, undergoes such deterioration, due to readily available atmospheric oxygen, water, and chloride [12–14]. On-demand maintenance of these structures not only preserves them but also reduces unnecessary costs and energy [15]. The chloride ion concentration in concrete is one of the most relevant parameters to estimate the risk of corrosion, and therefore predict the lifetime and maintenance cycle of RC structures [16–19].

In the present review, different techniques are summarized, reported so far for non-destructive in-situ measurement of chloride ion concentration in concrete. For more than two decades in-situ non-destructive measurement of chloride content in concrete has been reported in literature [20–22]. These ND techniques are characterized into two main approaches, i.e. electrochemical and electromagnetic. The description of these techniques along with their advantages and disadvantages are presented. In concrete, chlorides exists in different forms, namely free and bound chloride. Before describing the measurement techniques, it is important to introduce the states of the chloride ions in cementitious materials.

### 1.2. Types of chloride in concrete

Free chloride exists in ionic form in the pore solution and can diffuse towards the reinforcing steel through the pores. The traditional methods for free chloride ions determination involve extracting the pore solution from the cement-based materials by

applying pressure, or by leaching of chloride from the concrete sample by a solvent. It has been stated that these techniques are prone to considerable error. For example, destructive extraction of pore solution may overestimate the free chloride concentration by 30% to 200% [23].

The bound chloride ions are either chemically or physically attached to the hydration product such as calcium-silicate-hydrate (C-S-H) [24]. The chloride adsorption on the surface of C-S-H gives the physical binding of the chloride. It is due to electrostatic or Van der Waals forces between the chloride ions and the surface of the C-S-H. Such chloride ions are sensitive to the environmental conditions such as pressure and temperature. Chemical binding is the result of chemical reactions between chloride ions and cement hydration products such as tri-calcium aluminate ( $C_3A$ ) to form calcium chloroaluminate hydrate or Friedel's salt [25]. However, Friedel's salt is not the only phase responsible for chloride binding [26], other phases including Calcium-Silicate-Hydrate (C-S-H), hydration product of alite ( $C_3S$ ) and belite ( $C_2S$ ), [27,28] and the ferrite analogue of Friedel's salt also account for chloride binding [29–31]. The chemically bound chloride can be extracted in acidic environment [23,32].

### 1.3. Critical chloride content

Localized, or pitting corrosion in RC is initiated when the chloride ion concentration reaches a threshold value, which is also known as the critical chloride content,  $C_{crit}$  [33,34]. There are two different ways of defining  $C_{crit}$ : (1) based on theory i.e. the chloride ion concentration required for de-passivation of steel, (2) based on the visible deterioration of the concrete structure [34]. There are two stages of deterioration due to corrosion; initiation and propagation stage. In the initiation phase, no significant deterioration is observed, whereas in the propagation stage large deterioration and increase in corrosion rates are observed. According to the first definition the amount of chloride to initiate the propagation stage is  $C_{crit}$ , whereas, according to the second definition the amount of chloride to observe the visible deterioration in the propagation stage is  $C_{crit}$ .

Regarding the type of chloride responsible for pitting corrosion, some literature reports consider total chloride content [35,36] and others free chloride [34,37]. The free chloride ion concentration is mostly reported to be a better indicator for pitting corrosion. Several studies have been performed to evaluate  $C_{crit}$  [34], but there is no universal value so far, since it depends on several factors like pH, temperature, humidity, oxygen availability and steel concrete interface [34,38]. The heterogeneity of the concrete matrix can also affect the measurements. Angst et al. 2009 reviewed several conditions and mentioned values for critical chloride content reported so far [34]. According to this study, the ratio between the  $[Cl^-]$  and  $[OH^-]$  is found to be an appropriate expression form of  $C_{crit}$ , with the most accepted value of  $[Cl^-]/[OH^-] = 0.6$ .

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