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Analysis of chloride threshold from laboratory and field experiments in marine atmosphere zone

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HIGHLIGHTS

- Lower water to cement ratio means higher chloride threshold.
- Pozzolanic addition means lower chloride threshold.
- Field chloride thresholds are lower than laboratory chloride thresholds.
- There is a linear relationship between laboratory and field chloride thresholds.

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ABSTRACT

Studies focusing on chloride threshold analysis based on field experiments are still scarce. Although taking longer than laboratory experiments, they can help on setting chloride thresholds closer to realistic conditions. The present work analyses results from reinforced concrete specimens exposed in a marine atmosphere zone of the northeast coast of Brazil and also from specimens subjected to wetting and drying cycles in sodium chloride solution. After the process of corrosion had just been initiated, the concrete specimens were broken and the total and free chloride contents at the rebar level were measured and assumed as the chloride thresholds for starting corrosion. Results show that average total chloride threshold varies in a range between 1.82 and 2.45 (% cement weight) and between 0.88 and 1.58 (% cement weight) for laboratory and field exposure experiments, respectively. Environmental interaction contributes for these differences. On the other hand, a good correlation could be obtained between both experimental conditions, helping on transporting laboratory results to field conditions.

1. Introduction

Corrosion of reinforced concrete structures in marine environment starts after a certain level of chloride content is reached at the rebar surface. This chloride content is known as chloride threshold for depassivation of steel [1,2] and is associated with the end of the initiation period according to Tuutti's corrosion model [3]. Reliable estimations of this initiation period of corrosion, which depend on more accurate chloride transport estimations and also on more realistic chloride threshold values, are essential for more adequate service life analysis.

Chloride threshold depends on a significant number of parameters, which can be grouped in those related to material characteristics, environmental parameters or steel–concrete interface [4]. These aspects are discussed in the next subsections giving more attention to those with stronger relationship with the present work.

1.1. Influence of cement-based material characteristics on chloride threshold

Considering material characteristics that influence chloride threshold, cement composition and its binding ability [5,6], the use of mineral admixtures [7], water to cement ratio [8] and aging/curing conditions [9] are some of the main variables that are reported in literature as influencing the critical chloride content. These variables, in general, affect the amount of available chloride in the pore solution or the pH of the same solution, as well

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as the availability of moisture and oxygen at the reinforcement surface [10,11].

The amount of free chlorides depends on the binding capacity of cement matrix and also on the chemical equilibrium of this matrix. Bound chlorides content can be altered depending on changes of the water content in concrete porous network or concrete carbonation for example [12,13]. Regarding the binding ability of cement matrix, the content of C_3A and C_4AF seems to be the main parameter affecting bound chlorides [14], although these ions can also be physically bound on CSH surfaces [15].

The pH of pore solution represents the inhibitive effect of hydroxide ions against chloride induced corrosion [16] and it is influenced by the cement and mineral admixtures characteristics, which results in different chloride thresholds. Higher alkali contents in cement composition and more Portlandite formation means higher pH of pore solution and also higher buffering effect, that contributes for higher chloride thresholds. The use of mineral admixtures helps to decrease this alkalinity due to the pozzolanic reactions [17,18]. On the other hand, they can improve the physical and chemical binding ability in some cases. In the case of silica fume, the effect of alkalinity reduction seems to prevail and thus a reduction in chloride threshold was observed [19,20]. In the case of fly ash, some studies report a decrease in the tolerable chloride content [7,21,22], in contrast with others that did not report a significant influence of this admixture on chloride threshold [23] or reported higher tolerable chloride contents [24]. Similar behaviour was found in the case of blast furnace slag [21,22,24]. This apparent contradiction can be attributed to a competition between the alkalinity reduction promoted by fly ash or blast furnace slag [25], and the improvement of chemical and physical binding ability when using these admixtures [15], which can change depending on the admixture characteristics.

The availability of oxygen and moisture, besides the environmental influence, are related to the porosity of concrete. The water to binder ratio, the aging and curing of concrete, as well as the use of mineral admixtures influence concrete porosity and thus the availability of oxygen and moisture at the rebar surface. It has been reported that chloride threshold decreases as water to binder ratio increases, as a consequence of a higher availability of moisture and oxygen [10]. In a different way, but also related to the moisture content and concrete porosity, a relationship between chloride threshold and concrete resistivity has been proposed [26].

1.2. Influence of steel characteristics, steel–concrete interface and steel potential on chloride threshold

Steel composition and steel surface condition are material characteristics related to reinforcement that also influence the critical chloride content. Reinforcements with higher contents of carbon in their composition are more prone to corrosion [27], as well as mill-scaled bars [28–30]. This is explained by the detrimental and retarding effect of mill scale on the formation and performance of passive film [30]. The presence of ribs on reinforcement surface is another aspect that can influence chloride threshold [31,32], which can be explained by its contribution to entrap air bubbles or to generate internal exudation.

Taking into account the steel–concrete interface, the presence of voids can contribute to an easier pit formation [33]. This can be a consequence of rebar surface irregularities like the ribs, or of ineffective casting and compaction procedures. The lime layer deposited on reinforcement surface due to the hydration process makes the chloride threshold change depending on its buffering capacity of pH in the pit surroundings and on the effectiveness of this physical barrier for chloride diffusion [34–37]. Thus, it is expected that the richer and thicker are the lime layers, the higher are chloride thresholds.

The relationship between steel potential and chloride threshold was also studied and this is a way of considering the simultaneous influence of some of the previously outlined parameters on chloride threshold. It has been reported that chloride threshold is independent of the potential for values higher than −200 mV SCE (saturated calomel electrode) and it increases for more negative potentials following a linear relationship [23].

1.3. Influence of environmental parameters on chloride threshold

Considering environmental parameters, moisture content and oxygen supply are essential for the corrosion process and their rareness contribute for a higher chloride threshold [4,11]. In the specific case of concrete saturation, a rareness of oxygen can take place and, as a result, the corrosion initiation becomes more difficult to happen, contributing for higher chloride threshold measurements.

It has also been reported that an increase in temperature may decrease the bound chloride content making active corrosion easier to start [6,12,38]. An increase in temperature may also affect the activation energy required to cause passive film breakdown [4]. As a result, a lower chloride threshold is expected when temperature increases.

Concrete carbonation decreases the alkalinity in pore solution and also contributes to decrease the bound chlorides content [3,39,40]. This behaviour makes a lower chloride threshold be expected.

1.4. Chloride threshold representation

A common way for representing chloride threshold is thorough the total chloride content as a percentage of cement weight [7], which has the advantage of relatively easy determination procedures. Considering that only free chlorides represent a risk for starting corrosion, chloride threshold can also be represented by the free chloride content as a percentage of cement weight. This is sometimes criticised by the fact that bound chlorides can become free due to phenomena like carbonation, for example [4]. Another way for representing chloride threshold is by $[Cl^-]/[OH^-]$ ratio, which concerns the inhibitive role of hydroxides and it is considered a more accurate way for representing critical chloride content [41,42]. The chloride threshold as percentage of concrete weight is used in some countries, like the USA [43–45]. It is useful when there is not enough information about the concrete mixture, but it has the limitation of not taking into account the cement consumption and its alkalinity influence on depassivation process. Nevertheless, it may be pointed out that the first way of representation mentioned above is widely used to express chloride threshold in literature [11,31].

1.5. General evaluation of literature data

A significant number of studies that focus on chloride threshold analysis has been carried out since the sixties. These studies usually consider concrete, mortar or solutions that simulate the porous network solution of cement-based materials. Most of them are laboratory-based studies [1,2,5,28]. Studies focused on field exposure conditions that consider external sources of chloride from marine environment are not numerous [46,47]. Results from these studies show a significant scatter for chloride threshold. This happens as a consequence of the influencing parameters previously commented, as well as the experimental procedures adopted for determining chloride threshold. Moreover, the stochastic nature of the pitting corrosion initiation is another aspect that contributes to this variability [19].