



Experimental Study of Chloride Ion Diffusion in Reinforced Concrete for Durability Prediction in Marine Environments

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Abstract. Reinforced concrete is the primary material used in coastal and marine infrastructure but is highly susceptible to chloride ion (Cl^-) diffusion, which accelerates reinforcement corrosion and shortens service life. This study experimentally investigates the vertical diffusion of chloride ions in reinforced concrete exposed to simulated seawater, with a focus on the effects of gravitational and convective transport. Eighteen cylindrical specimens ($\varnothing 75 \times 150$ mm) with embedded steel reinforcement and a 37.5 mm concrete cover were immersed in a 3.5% NaCl solution for 5–30 days. Chloride diffusion was determined using the AgNO_3 colorimetric method (0.1 M) in accordance with BS EN 14629:2007, and diffusion depth was quantified via digital image analysis using ImageJ software. The results revealed four distinct phases of chloride diffusion: (a) initial linear growth (5–15 days), (b) sharp exponential increase (17–21 days), (c) temporary stabilization (21–24 days), and (d) further increase beyond 22 mm at 30 days. Vertical diffusion progressed more rapidly due to gravitational and convective mechanisms, indicating higher risks in splash zones and wet–dry transition regions. These findings indicate that chloride ion diffusion in the vertical and horizontal directions exhibits distinct transport mechanisms in reinforced concrete. Therefore, these directional diffusion parameters should be explicitly considered in the formulation of service-life prediction models for concrete.

Keywords: Reinforced concrete, corrosion initiation, vertical diffusion, colorimetry, artificial seawater.

1 Introduction

Reinforced concrete is the most widely used construction material in modern infrastructure [1][2], especially in buildings located in coastal areas or exposed to marine environments [3][4]. The primary advantage of concrete is its strength in resisting compressive loads and its ability to protect steel reinforcement from corrosion

by forming a passive layer due to its high alkalinity [5][6]. However, one major weakness of reinforced concrete is its susceptibility to chloride ion (Cl^-) diffusion, which can lead to premature structural damage [7][8][9].

Chloride ions can enter concrete through diffusion, migration, and convection mechanisms [1][5]. When the chloride concentration reaches the steel reinforcement and exceeds a critical threshold ($\sim 0.4\%$ by weight of cement), the passive layer is broken, leading to electrochemical corrosion of the steel [5][6]. Corrosion products (rust) have a larger volume than the original steel, causing internal pressure that leads to cracking, spalling, and structural degradation [4]. This condition is particularly dangerous for buildings near the sea, bridges, docks, and harbors, where chloride ion exposure is high [10][11].

Previous studies have examined chloride ion diffusion in concrete using various methods such as the Rapid Chloride Migration Test (RCMT), ponding tests, and colorimetric methods using AgNO_3 (Silver Nitrate) solutions [12][13][14]. These studies generally report that chloride diffusion is progressive, with a linear pattern in the early phase and exponential growth once the concrete's pores become saturated. Subsequent studies have shown that concrete quality, water-cement ratio (w/c), and the presence of microcracks significantly affect the rate of chloride diffusion [14][15].

However, there is a research gap in understanding the difference in chloride diffusion rates in the vertical and horizontal directions. Most previous studies have focused on average diffusion profiles [16], without distinguishing the orientation of diffusion [17], even though the vertical direction could potentially be the dominant path due to gravitational and convective flow contributions [18].

This study aims to investigate the visual changes in concrete specimens caused by chloride ion diffusion using the AgNO_3 colorimetric method and to measure the chloride ion diffusion depth in reinforced concrete using digital image analysis (ImageJ). It also analyzes the relationship between immersion time and chloride ion diffusion. This research is expected to contribute to the literature on reinforced concrete durability in marine environments and form the basis for developing strategies to extend the service life of such structures.

2 Research Methodology

2.1 Materials and Specimens

Reinforced concrete specimens were prepared using Portland Cement Type I, coarse aggregate, fine aggregate, and water with weight proportions of 28.04%, 36.77%, 24.51%, and 10.65%, respectively. Plain steel reinforcement with a diameter of 10 mm was placed at the center of each specimen with a concrete cover of 37.5 mm from the outer surface.

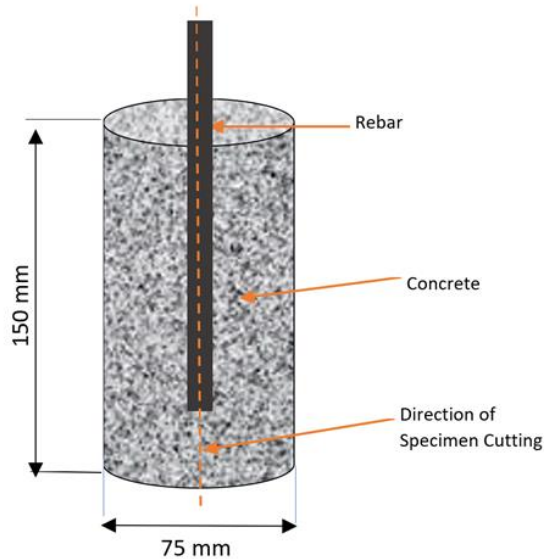


Figure 1. Dimensions and sizes of the test specimens

Eighteen cylindrical specimens ($\varnothing 75 \times 150$ mm) were prepared (Figure 1). After casting, all specimens were cured for 7 days at room temperature to simulate seawater exposure. After curing, the samples were immersed in a 3.5% sodium chloride (NaCl) solution

2.2 Immersion and Chloride Ion Exposure

All specimens were immersed in a 3.5% NaCl solution after the curing process. For the chloride colorimetric method testing, measurements were taken within the 9-30 day period.

2.3 AgNO_3 Colorimetric Method

Chloride ion diffusion was analyzed based on BS EN 14629:2007 using the AgNO_3 colorimetric method. After immersion periods, the specimens were cut vertically, and a 0.1 M AgNO_3 solution was sprayed on the cut surface. The color change (light/dark) indicated the chloride-contaminated zone. The sprayed surface was photographed using a digital camera, and the penetration depth was measured using ImageJ software (open source). The data from the measurements were analyzed statistically using Microsoft Excel and represented in the form of a graph relating immersion time to chloride ion diffusion depth

3 Results and Discussion

3.1 Visual Condition of Specimens During Immersion

The specimens were immersed in the 3.5% NaCl solution for the specified immersion periods, up to 30 days. Visual changes in the specimens during immersion are shown in Figure 2.



Figure 2. Visual appearance of the specimen immersed in artificial seawater

The specimen, positioned 30 cm away from the artificial seawater and immersed for 30 days, is shown in Figure 3.

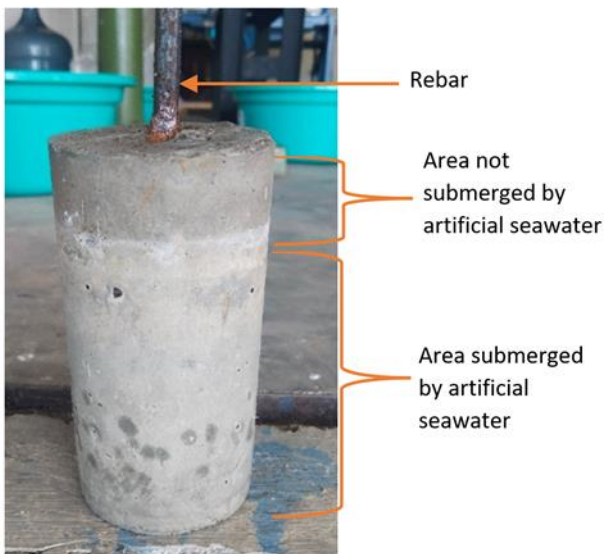


Figure 3. Visual appearance of the specimen after being immersed for 30 days

3.2 Chloride Ion Diffusion Measurements

The study involved immersing 18 reinforced concrete specimens in artificial seawater for periods between 5 and 30 days. Chloride chloride diffusion was tested by cutting the specimens in the vertical direction and spraying the surface with AgNO_3 solution. The surface was photographed and measured using ImageJ software. The results of the chloride ion penetration in the vertical direction are shown in Figure 4.

During immersion in the 3.5% NaCl solution, visual changes occurred on the concrete surface. After spraying with AgNO_3 , the areas contaminated with chloride ions changed color to light, while the chloride-free areas remained dark (Figure 4). This color change confirms the penetration of chloride ions into the concrete matrix

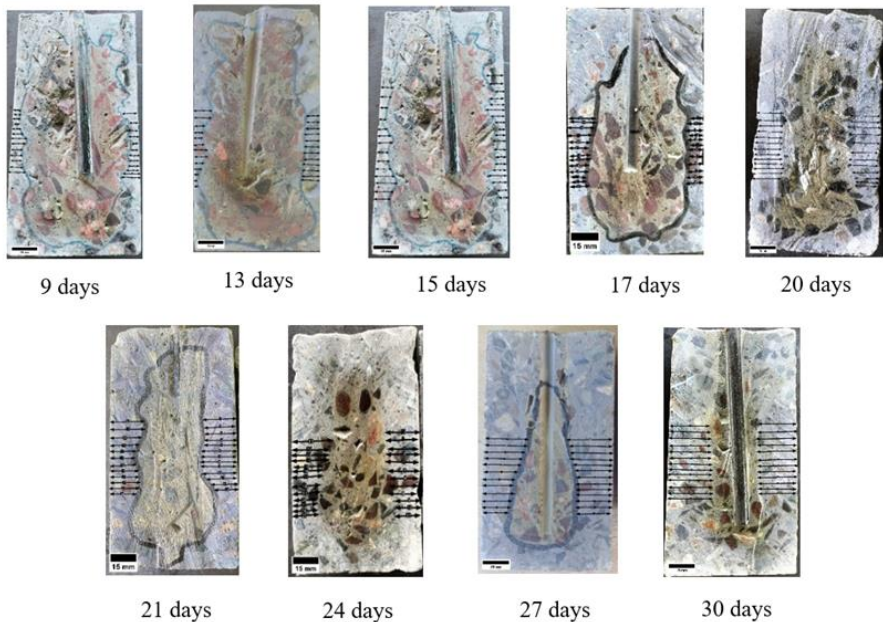


Figure 4. Visual appearance of the specimen after immersion and chloride ion exposure, the areas of chloride contamination are shown after spraying with AgNO_3 .

Figure 4. generally shows that chloride ion diffusion in reinforced concrete in the area above the seawater surface occurs more rapidly due to capillary action [19], evaporation [20], an unsaturated environment [21], and wet-dry cycles that accelerate chloride migration into the concrete [22]. These factors make the zone above the seawater surface more vulnerable to corrosion compared to the fully submerged zone.

3.3 Analysis of the Relationship Between Immersion Time and Chloride Diffusion

The measurements using ImageJ show that the depth of chloride ion diffusion in the vertical direction increases with the duration of immersion, as plotted and presented in Figure 5.

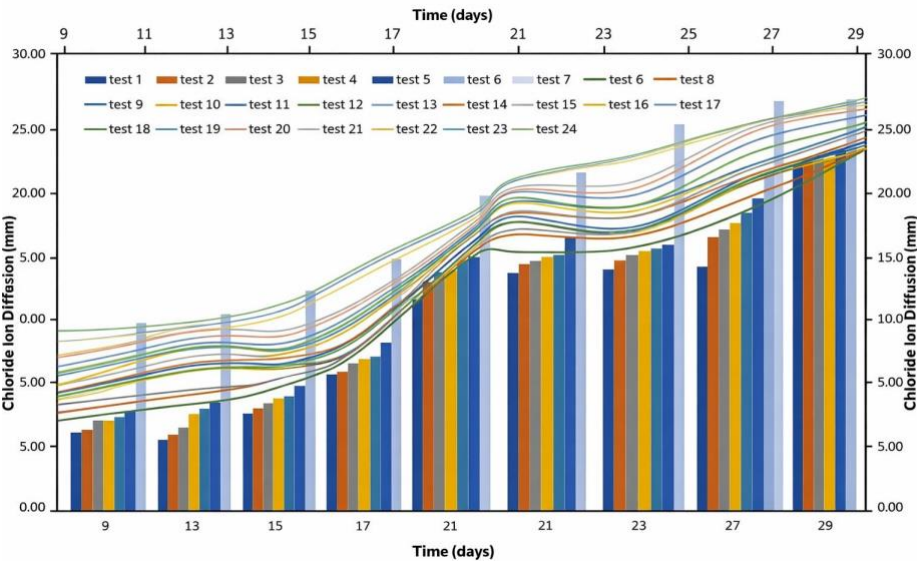


Figure 5. Results of measuring the chloride ion diffusion depth in concrete

The graph in Figure 5. shows a trend of increasing chloride ion penetration over time. From day 9 to day 15, the penetration increase is linear and slow. After day 17, the penetration sharply accelerates, exhibiting exponential behavior. The average chloride ion diffusion exceeds 20 mm by day 30.

Tests 5, 6, and 25 exhibit higher penetration compared to the others. This variation may be attributed to differences in concrete quality, moisture content, density, or the presence of microcracks. Chloride ion diffusion in concrete increases significantly with the immersion time. The exponential trend indicates that protection against chloride ingress becomes increasingly crucial as the structure ages.

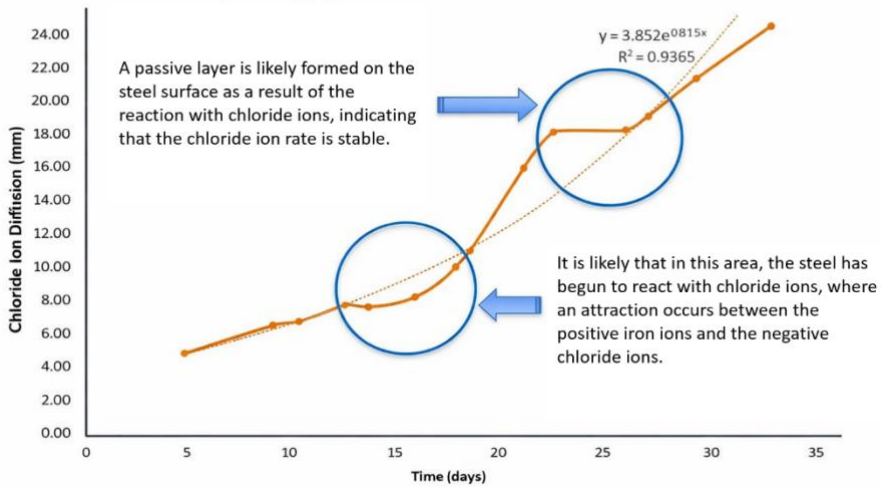


Figure 6. Relationship between chloride ion diffusion and immersion time of reinforced concrete

The graph in Figure 6. shows that vertical chloride ion diffusion gradually increases, reaching approximately 22 mm by day 30. The curve exhibits four main phases: Initial Linear Growth (5–15 days): a gradual increase (7–10 mm); Rapid Spike (17–21 days): a sharp increase in penetration (>18 mm); Temporary Stabilization (21–24 days): a plateau around 18–19 mm; Further Increase (25–30 days): penetration exceeding 22 mm. This pattern aligns with the chloride diffusion model in concrete, where initial penetration is dominated by the concrete's resistivity, followed by an exponential increase once the pores become saturated [22] and the formation of new diffusion paths [23][24].

Vertical diffusion is more influenced by gravitational forces and convective flow of the solution [25][26], Ion migration in the vertical direction is enhanced by the movement of the solution following the direction of gravity, so the transport rate is determined by the concentration gradient [27][28].

Vertical chloride ion diffusion greater than 22 mm within 30 days indicates a high risk for reinforced concrete with a thin cover (<25 mm). If chloride ions reach the steel reinforcement, the passive layer will be damaged, triggering electrochemical corrosion [29][3][8]. The critical chloride threshold for the conservation and service life design of reinforced concrete structures, which marks the initiation of steel corrosion, is 0.2 - 0.4% by weight of cement [30][31]. Under the conditions of this study, the risk of early corrosion in marine structures or piers can occur sooner than the designed service life. This suggests that the durability of reinforced concrete structures in marine environments could be significantly shorter if mitigation measures are not applied.

4 Summary

Chloride ion diffusion in reinforced concrete immersed in a 3.5% NaCl solution exhibits a progressive trend characterized by four distinct phases: initial linear growth (5–15 days), an exponential spike (17–21 days), temporary stabilization (21–24 days), and a subsequent increase, with penetration depths exceeding 22 mm by day 30.

Vertical chloride ion diffusion is significantly influenced by gravitational and convective effects, indicating that diffusion orientation plays a critical role in the ion transport mechanism. Therefore, the orientation of chloride ion diffusion should be explicitly considered in service-life prediction modeling for concrete.

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