

Article

An Experimental Study on the Effects of Oxygen and Moisture Transport Control on Steel Corrosion in Reinforced Concrete Structures

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Abstract

In this study, the effects of suppressing oxygen and moisture diffusion through the application of surface finishing materials on the initiation and progression of steel corrosion in concrete were comparatively evaluated. To this end, the type of binder and the chloride ion content were selected as the main variables, and the corrosion behavior of embedded steel was analyzed using the Half-Cell Potential Method, which enables quantitative assessment of electrochemical changes during the early stage of corrosion. Through this approach, the study aimed to provide fundamental data for establishing rational criteria for the intrinsic chloride ion content in cement. The results showed that the incorporation of ground granulated blast-furnace slag and the application of a coating were effective in delaying or reducing steel corrosion through chloride ion immobilization and the suppression of oxygen and moisture diffusion, respectively. However, under the condition of using ordinary Portland cement (OPC) alone, the likelihood of corrosion was found to increase significantly when the chloride ion content exceeded the critical threshold.

Keywords: reinforced concrete; steel corrosion; chloride; half-cell potential method; ordinary Portland cement; ground granulated blast-furnace slag

1. Introduction

1.1. Background and Research Objectives

With the intensification of global warming and the climate crisis driven by greenhouse gas emissions, the Paris Agreement was adopted in December 2015 to strengthen international efforts to limit the increase in the global average temperature to 1.5 °C [1]. In response to this global movement, Korea established the 2030 National Greenhouse Gas Reduction Roadmap under the Framework Act on Low Carbon, Green Growth, enacted in 2010, and later set a national target of achieving carbon neutrality by 2050.

Cement, the primary binder in concrete, is manufactured by blending and grinding limestone (CaCO_3), the main raw material, with clay minerals containing SiO_2 , Al_2O_3 , and Fe_2O_3 , followed by high-temperature calcination above 1450 °C. In cement production, the clinker manufacturing process is responsible for approximately 93% of the total CO_2 emissions. Of these emissions, around 33% result from fossil fuel combustion, whereas approximately 60% arise from the decomposition of limestone. Consequently, the production of 1 ton of cement is known to emit approximately 0.8 tons of CO_2 [2,3].

The cement and concrete sector is recognized as one of the major carbon-intensive industries worldwide, accounting for approximately 7% of total CO_2 emissions [4]. Its global



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CO₂ emissions exceed 2.5 Gt annually, primarily originating from limestone calcination during clinker production and from fuel combustion required for high-temperature kiln operations [5,6].

In response, the cement industry has been establishing various research and implementation strategies to contribute to the achievement of carbon neutrality by 2050. One such strategy involves the development and application of technologies that replace fossil fuels with alternative fuels, including waste synthetic resins [7]. Because waste synthetic resins exhibit lower CO₂ emissions per unit of calorific value, their use as alternative fuels in cement production can contribute to CO₂ emission reduction [8] while also offering benefits for waste management [9]. Nevertheless, concerns have been raised that chloride ions (Cl[−]) contained in waste synthetic resins may be introduced into the cement manufacturing process, leading to an increase in the chloride content of cement.

In this context, the chloride content in cement has become an important quality control parameter for ensuring the durability of reinforced concrete structures. Several standards specify limits or reporting requirements for chloride content in cement, because excessive chloride incorporation can increase the risk of passive film breakdown and chloride-induced corrosion of reinforcing steel [10–22]. Therefore, it is necessary to evaluate whether chloride ions internally incorporated into cement can directly lead to reinforcing steel corrosion and to establish rational criteria considering the actual corrosion environment of concrete. As summarized in Table 1, chloride content limits for concrete and cement differ among countries, depending on the regulatory system, concrete type, exposure condition, and whether the limit is expressed per unit volume of concrete or by mass of binder.

Table 1. Comparison of chloride content limits in concrete and cement by country [10].

Category	Korea	Japan	China	United States	European Union
Limit for general reinforced concrete	0.30 kg/m ³	0.30 kg/m ³	0.30% by mass of binder	0.30% by mass of binder (wet condition), 1.0% by mass of binder (dry condition)	0.20% by mass of binder (wet condition), 0.30% by mass of binder (dry condition)
Limit for prestressed concrete	0.30 kg/m ³	0.30 kg/m ³	0.30% by mass of binder	0.06% by mass of binder	0.10% by mass of binder
Chloride limit in cement	–	350 ppm	600 ppm	–	1000 ppm
Chloride regulation system	Total chloride content	Total chloride content	Total chloride content in hardened concrete	Total chloride content in hardened concrete	Total chloride content in hardened concrete

In general, the highly alkaline pore solution of concrete, typically having a pH of approximately 12.5–13.5, promotes the formation of a thin passive film on the surface of reinforcing steel. This passive film substantially suppresses the anodic dissolution of iron and enables reinforcing steel to remain thermodynamically unstable but kinetically protected within concrete [23]. However, when a sufficient concentration of chloride ions reaches the steel–concrete interface, the passive film can become locally destabilized at susceptible sites. Chloride-induced depassivation is therefore governed not solely by the total chloride content of concrete but also by the local chloride-to-hydroxyl ion ratio, binder composition, pore-solution chemistry, steel surface condition, and characteristics of the steel–concrete interface [24–26].

Following local breakdown of the passive film, active anodic sites are formed within the depassivated regions, whereas the surrounding passive steel surface acts predominantly as a cathodic area. At the anodic sites, iron is dissolved according to Equation (1):



The electrons released by the anodic reaction flow through the reinforcing steel toward the cathodic regions. Under the alkaline conditions generally present in concrete, dissolved oxygen is reduced in the presence of water according to Equation (2):



Accordingly, moisture in the concrete pore system acts as an electrolyte that enables ionic transport between the anodic and cathodic regions, while oxygen supports the cathodic reaction. The ferrous ions generated at the anodic sites subsequently undergo hydrolysis and oxidation to form iron hydroxides and oxides. Hydrolysis within a developing pit can locally decrease the pH, while the migration and accumulation of chloride ions maintain electrical neutrality and promote further dissolution of iron. Consequently, chloride-induced corrosion can develop as a self-sustaining localized process, even though most of the surrounding reinforcing steel remains passive [27,28].

This corrosion mechanism differs from the relatively widespread depassivation generally associated with carbonation. Chloride-induced corrosion predominantly develops in the form of localized pitting, which can cause substantial penetration and loss of the steel cross-sectional area before extensive corrosion damage becomes visible at the concrete surface. As corrosion progresses, the formation and accumulation of expansive corrosion products generate tensile stresses in the surrounding concrete, ultimately resulting in cracking, delamination, and spalling of the concrete cover [29,30].

The corrosion behavior of reinforcing steel is also influenced by the binder system. The incorporation of GGBS may alter the pore structure, electrical resistivity, pore-solution chemistry, and physical and chemical binding of chloride ions [31]. Therefore, OPC- and GGBS-based concrete containing the same total chloride content may not necessarily exhibit the same concentration of free chloride ions at the steel surface or the same electrochemical corrosion response. These competing effects should be considered when evaluating the corrosion risk associated with internally incorporated chloride ions.

However, the presence of chloride ions above a prescribed reference value does not necessarily result in immediate or continuous corrosion. Corrosion propagation depends on the simultaneous availability of moisture and oxygen, as well as on concrete resistivity, temperature, and the spatial separation of anodic and cathodic regions. In building structures, concrete surfaces are frequently covered with finishing materials. A surface coating may reduce the exchange of oxygen and moisture between the concrete and the external environment and thereby modify the electrochemical conditions governing reinforcement corrosion. Conversely, a low-permeability coating may also restrict the drying of concrete and retain moisture already present within the pore structure. Therefore, the influence of a coating cannot be attributed solely to the prevention of external moisture ingress, and its effect should be interpreted in relation to the internal moisture condition and oxygen availability of the concrete.

Furthermore, the initiation of reinforcement corrosion and the critical chloride threshold may vary depending not only on the compressive strength of concrete, but also on the binder content, water-to-binder ratio, binder composition, alkalinity of the pore solution, and chloride-binding capacity. Therefore, different corrosion behaviors may occur at the same chloride content in concretes with different strength levels and binder systems. In this study, concrete with a specified compressive strength of 24 MPa was selected to represent normal-strength concrete commonly used in building structures in Korea. Compared with high-strength concrete, concrete at this strength level may have a relatively lower binder content and alkaline reserve. It was therefore selected to evaluate the effects of binder type and surface coating on reinforcement corrosion under conditions involving internally admixed chlorides.

Accordingly, this study investigates the combined effects of binder type and epoxy surface coating on the chloride-induced corrosion behavior of reinforcing steel embedded in concrete containing internally admixed chloride ions. OPC concrete and concrete containing 40% GGBS were examined at different initial chloride contents, both with and without an epoxy surface coating. The corrosion behavior was evaluated to determine whether the surface coating modified the initiation and subsequent development of reinforcement corrosion under the investigated exposure conditions.

1.2. Related Works

The major deterioration mechanisms affecting the durability of reinforced concrete structures can be broadly classified into deterioration of the concrete itself and corrosion of reinforcing steel. Sulfate attack and freeze–thaw cycles primarily cause physical and chemical deterioration of the concrete, thereby reducing the durability of the structure. In contrast, carbonation and chloride attack are representative deterioration mechanisms that can induce reinforcement corrosion by destabilizing the passive film formed on the steel surface. In particular, chloride-induced corrosion of reinforcing steel is one of the major deterioration mechanisms that directly affects the long-term durability and service life of reinforced concrete structures, and has therefore been extensively investigated.

Furthermore, reinforcement corrosion can lead to a reduction in the effective cross-sectional area of reinforcing steel and deterioration of the structural performance of reinforced concrete members. Crespi et al. [32] demonstrated that corrosion-induced deterioration of reinforcement can significantly affect the seismic capacity and failure mechanisms of existing reinforced concrete bridges, highlighting the importance of appropriate durability assessment and maintenance strategies.

Most previous studies have focused on chloride ions introduced from external environments, particularly marine exposure and de-icing salts, and have evaluated chloride transport and diffusion through concrete, the critical chloride content at the reinforcement depth, and the initiation and subsequent development of reinforcement corrosion [26]. Consequently, a substantial body of research has been accumulated on the penetration and diffusion of externally supplied chlorides and the critical chloride content associated with the initiation of reinforcing steel corrosion.

In contrast, studies investigating the effects of internally admixed chlorides originating from constituent materials, such as cement, on reinforcing steel corrosion remain relatively limited. Unlike chlorides that penetrate from external environments, internally admixed chlorides are present in the concrete from the early stages of cement hydration and may therefore interact physically and chemically with hydration products, thereby influencing the pore-solution chemistry and corrosion environment surrounding the reinforcing steel. Pradhan and Bhattacharjee [33] investigated the corrosion behavior of reinforcing steel in concrete containing internally admixed chlorides using OPC, Portland pozzolana cement (PPC), and Portland slag cement (PSC). Their results showed that the cement type significantly affected the free and total chloride contents, electrical resistivity of concrete, half-cell potential, and corrosion current density. In particular, PSC concrete exhibited a relatively delayed onset of corrosion. Kim and Ann [34] directly compared reinforcement corrosion induced by internally admixed and externally supplied chlorides and reported that the critical chloride concentration varied depending on the mode of chloride introduction. These findings suggest that the corrosion behavior associated with internally admixed chlorides may not necessarily be interpreted using the same criteria established for externally penetrating chlorides.

The effects of supplementary cementitious materials on chloride penetration and reinforcement corrosion have also been extensively investigated. Yeau and Kim [35] eval-

uated the chloride and corrosion resistance of concrete containing ground granulated blast-furnace slag (GGBS) using rapid chloride permeability, accelerated chloride diffusion, and reinforcement corrosion tests. They reported that the incorporation of GGBS improved resistance to chloride penetration and reinforcement corrosion. Jiang et al. [36] compared macrocell corrosion behavior under carbonation, internally admixed chloride, and external chloride penetration conditions using concretes with different binder systems. Their results showed that the detrimental effects of internally admixed chlorides were relatively lower in concrete containing slag or fly ash than in OPC concrete, which was attributed primarily to the enhanced chloride-binding capacity associated with the use of supplementary cementitious materials. These findings indicate that, even at the same total chloride content, the amount of free chloride available at the steel–concrete interface and the resulting electrochemical corrosion behavior may vary depending on the binder composition.

Surface coatings have also been widely investigated as a means of improving the durability of reinforced concrete structures exposed to chloride-bearing and other aggressive environments. However, most previous studies have evaluated surface coatings primarily as physical barriers that inhibit the ingress of chloride ions and moisture from the external environment. Al-Zahrani et al. [37] investigated the effects of various waterproofing coatings on reinforcement corrosion and the transport properties of concrete and reported that polymer-based surface coatings were effective in delaying the initiation of reinforcing steel corrosion. Similarly, Almusallam et al. [38] evaluated various surface coating systems in terms of water absorption, chloride permeability, and chloride diffusion and reported that epoxy- and polyurethane-based coatings exhibited relatively high resistance to chloride transport. A summary of representative previous studies related to chloride-induced reinforcement corrosion, internally admixed chlorides, binder composition, and surface coatings is presented in Table 2.

Table 2. Comparison of previous studies and the present study on chloride-induced corrosion of reinforcing steel in concrete.

Ref.	Binder	Chloride Condition	Surface Coating	Key Findings
Angst et al. [26]	Mainly OPC and various binders	Mainly external chloride	-	Critical chloride content varies substantially with materials, exposure, and test conditions
Pradhan and Bhattacharjee [33]	OPC, PPC, PSC	Internally admixed	-	Cement type affected corrosion initiation; PSC showed a longer initiation period
Kim and Ann [34]	Cementitious system	Internal/external	-	Internal and external chloride conditions exhibited different thresholds
Yeau and Kim [35]	OPC, GGBS	External chloride	-	GGBS improved chloride penetration and corrosion resistance
Jiang et al. [36]	OPC, slag, fly ash	Internal/external	-	Slag and fly ash reduced the detrimental effect of internally admixed chloride
Al-Zahrani et al. [37]	Type I Portland cement	External exposure	Polymer-based and cement-based coatings	Surface coatings delayed corrosion initiation
Almusallam et al. [38]	ASTM Type V Portland cement	External chloride	Epoxy, PU, acrylic, etc.	Epoxy and polyurethane showed high resistance to chloride transport
Present study	OPC, GGBS	Internally admixed	Uncoated/epoxy-coated	Combined effects of binder type and coating under internally admixed chloride condition

Overall, previous studies have extensively investigated the penetration of externally supplied chlorides and the resulting reinforcement corrosion, while the effects of internally admixed chlorides, binder composition, and surface coatings have generally been examined as individual factors. However, relatively few studies have systematically investigated the combined effects of these factors together. In particular, the influence of epoxy surface coatings on the electrochemical corrosion behavior of reinforcing steel in OPC and GGBS concrete containing internally admixed chlorides has not yet been sufficiently clarified. Therefore, the present study comparatively evaluates the corrosion behavior of reinforcing steel in OPC and GGBS concrete containing internally admixed chlorides under uncoated and epoxy-coated conditions. Particular emphasis is placed on changes in half-cell potential and the corrosion condition of the reinforcing steel after exposure in order to clarify the combined effects of binder type and surface coating on reinforcement corrosion.

2. Experimental Program and Methods

2.1. Experimental Factors and Levels

This study comparatively evaluated the influence of binder type, chloride ion incorporation level, and the presence or absence of surface coating on reinforcing steel corrosion. Although KDS 14 20 40 (Durability Design Standard for Concrete Structure) [13] specifies a minimum compressive strength of 30 MPa for concrete exposed to the ES1 exposure class, the 24 MPa-class concrete used in this study was not selected to represent or satisfy the durability requirements of the ES1 exposure condition. Rather, 24 MPa-class normal-strength concrete was intentionally selected as an experimental condition to more sensitively evaluate the effects of internally incorporated chloride ions. In general, at a given chloride content per unit volume of concrete, an increase in binder content may reduce the chloride-to-binder ratio and enhance both chloride-binding and alkaline-buffering capacities. Therefore, the relatively lower binder content associated with the 24 MPa-class concrete was considered suitable for examining the effects of binder type and surface coating on corrosion behavior under internally admixed chloride conditions. Reinforcing steel corrosion was monitored using the half-cell potential method to evaluate electrochemical changes associated with corrosion probability. The experimental factors and levels are summarized in Table 3.

Table 3. Experimental factors and their levels.

Experimental Factors	Levels
Design compressive strength	24 MPa
Binder	OPC, GGBS *
Binder content	340 kg/m ³
SCMs ** replacement level	40%
Chloride ion content	0, 1.2, 2.4 kg/m ³
Finishing material	No coating (N.C), with coating (C)
Curing method	Air curing
Compressive strength	7, 28 days
Corrosion assessment	Natural potential monitoring using an embedded reference electrode
Steel corrosion	Measurement of the corrosion area by image analysis
Determination of Corroded Area	

* Ground granulated blast-furnace slag. ** Supplementary cementitious materials.

2.2. Materials and Mix Proportions

The concrete mixtures were designed using two binder systems: one containing only ordinary Portland cement (OPC) and another in which 40% of the OPC was replaced with ground granulated blast-furnace slag (GGBS). The detailed mix proportions of the concrete

are presented in Table 4. Considering that the threshold chloride ion concentration for the initiation of reinforcing steel corrosion is 1.2 kg/m^3 , the initial chloride ion contents were set to 0, 1.2, and 2.4 kg/m^3 . The corresponding amounts of NaCl (Samchun Pure Chemical Co., Ltd., Pyeongtaek, Gyeonggi-do, Republic of Korea) required to achieve each target chloride ion content were calculated and incorporated into the mixtures. The target slump and air content of the concrete were set to $180 \pm 25 \text{ mm}$ and $4.5 \pm 1.5\%$, respectively. The dosages of the polycarboxylate-based water-reducing admixture and air-entraining (AE) agent were adjusted to achieve the target slump and air content.

Table 4. Mix proportions of concrete.

Mixture	W/B (%)	S/a (%)	Unit Weight (kg/m^3)					
			W	OPC	GGBS	S	G	NaCl
OPC-0NaCl	49.1	49.3	167	340	0	891	924	0
OPC-1.2NaCl	49.1	49.3	167	340	0	891	924	1.98
OPC-2.4NaCl	49.1	49.3	167	340	0	891	924	3.96
BS40-0NaCl	49.1	49.3	167	204	136	886	918	0
BS40-1.2NaCl	49.1	49.3	167	204	136	886	918	1.98
BS40-2.4NaCl	49.1	49.3	167	204	136	886	918	3.96

2.3. Specimen Preparation

For each mixture, two specimens were prepared considering the presence or absence of a surface coating. Specimens were fabricated using $100 \times 100 \times 400 \text{ mm}$ molds, and D19 deformed reinforcing bars (SD400) were embedded to ensure a concrete cover depth of 20 mm from the casting surface. To eliminate the influence of the initial corrosion condition of the reinforcing bars on the experimental results, corrosion products on the bars were removed by immersion in a 10% ammonium citrate solution followed by polishing before embedding them in concrete.

In this study, a surface coating was applied to the specimens to evaluate the effect of oxygen and moisture diffusion control on reinforcing steel corrosion. Therefore, half-cell potential measurements through the concrete surface were not possible. Accordingly, instead of using a commonly employed saturated copper/copper sulfate (Cu/CuSO_4) reference electrode, a lead reference electrode was embedded inside the concrete. To evaluate only chloride-induced corrosion of the reinforcing steel, the reference electrode was positioned with sufficient spacing from the reinforcing bar to minimize the influence of electrochemical galvanic corrosion. The dimensions of the corrosion test specimen are shown in Figure 1, and the mold was prepared by pre-embedding the reinforcing bar and reference electrode before concrete casting, as shown in Figure 2.

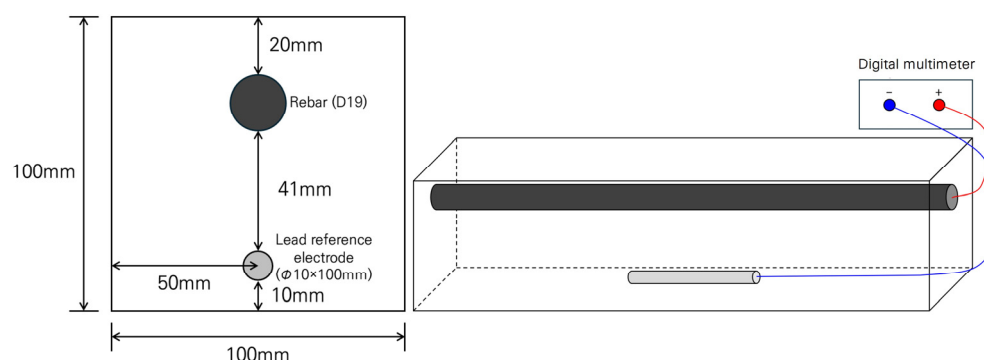


Figure 1. Specifications of reinforced concrete specimens for corrosion testing.



Figure 2. Example of a mold with reinforcing steel and a reference electrode pre-embedded prior to concrete casting.

After the concrete was cast into the molds in which the reinforcing bar and lead reference electrode had been embedded, sealed curing was conducted to prevent moisture evaporation from the specimen surface. The specimens were demolded 24 h after casting and subsequently cured in a thermo-hygrostat chamber at 20 °C and 60% RH.

In addition, an epoxy coating was applied to the specimen surface to comparatively evaluate the effects of oxygen and moisture diffusion control on reinforcing steel corrosion. However, if the epoxy coating is applied immediately after demolding, coating delamination and a reduction in adhesion may occur owing to the high moisture content inside the concrete. Therefore, the epoxy coating (EPOCOAT, Samhwa Paints Industrial Co., Ltd., Ansan, Gyeonggi-do, Republic of Korea) [39] was applied after 28 days of curing under constant temperature and humidity conditions. The coating was applied in two coats using a roller to achieve a final dry film thickness of 40–80 µm. The experimental timeline of this study is presented in Figure 3.

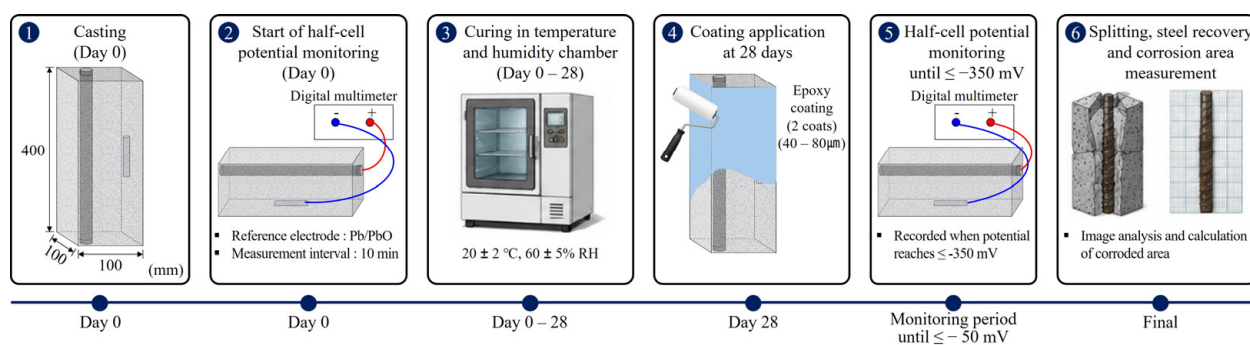


Figure 3. Experimental timeline.

2.4. Test Methods

2.4.1. Slump and Air Content Test

Workability was measured immediately after mixing using a slump test. The air content was measured according to ASTM C231 [40]. Slump and air content were mea-

sured once for each concrete batch as fresh-concrete quality-control parameters; therefore, statistical dispersion was not evaluated for these properties.

2.4.2. Mechanical Properties

The compressive strength test was conducted in accordance with KS F 2405 [41] using a universal testing machine at a loading rate of 0.6 MPa/s. For each mixture, three samples were tested, and the average value was calculated to determine the compressive strength.

2.4.3. Air Permeability Test Using the Torrent Method

To indirectly evaluate the gas transport characteristics of the concrete surface and the oxygen-barrier effect of the coating, an air permeability test was conducted using the Torrent method. The test was performed on uncoated and coated specimens prepared under identical mixture and curing conditions. To minimize the influence of the relatively porous casting surface, the air permeability coefficient was measured on the surface opposite to the casting face using a Torrent permeability tester.

2.4.4. Evaluation of Reinforcing Steel Corrosion by Half-Cell Potential Measurements

To determine the occurrence of reinforcing steel corrosion, half-cell potential measurements were conducted on the reinforced concrete specimens in accordance with ASTM C876 [42]. Two specimens were tested for each mixture condition. The measurement setup is shown in Figure 4. The corrosion evaluation criteria specified in ASTM C876 are based on the Cu/CuSO₄ reference electrode, as summarized in Table 5. However, in this study, the half-cell potential was measured using a Pb/PbO combined reference electrode. Therefore, the measured potentials were converted to equivalent potentials relative to the Cu/CuSO₄ reference electrode using the conversion equations provided in the Japan Society of Civil Engineers standard, Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete (JSCE-E601-2000) (2002) [43], as shown in Table 6.

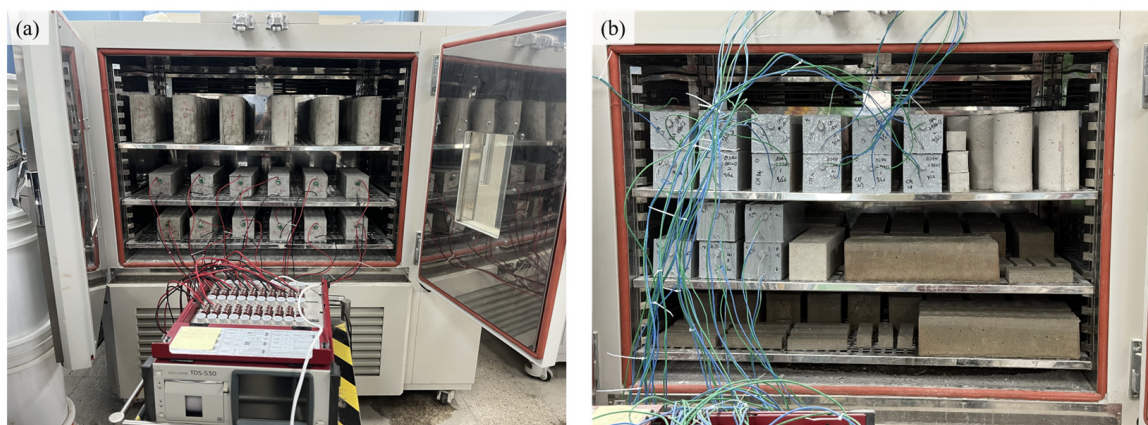


Figure 4. Half-cell potential measurement setup for reinforced concrete specimens: (a) before coating application and (b) after coating application.

Table 5. ASTM criteria for corrosion of steel in concrete.

Cu/CuSO ₄ Half-Cell	Probability of Corrosion Activity
More positive than −200 mV	>90% probability of no corrosion occurring
−200 to −350 mV	Probability of corrosion uncertain
More negative than −350 mV	>90% probability of corrosion occurring

Table 6. Conversion equation for half-cell potentials measured using a lead electrode.

Type of Reference Electrode	Conversion Equation
Lead electrode	$-799 + 0.24 \times (t - 25)$

t: temperature.

The half-cell potential was measured at 10 min intervals to clearly identify the initiation time of reinforcing steel corrosion. Corrosion was judged to have occurred when the measured potential changed abruptly or decreased to -350 mV or lower. At this point, the specimens were fractured, and the corrosion condition of the reinforcing steel was visually examined.

2.5. Measurement Method for Corroded Area of Reinforcing Steel

The corroded area of the reinforcing steel was measured after the completion of the half-cell potential measurements. The specimens were split, and the reinforcing bars were extracted, followed by the removal of concrete adhering to the bar surface. Subsequently, transparent cellophane film was tightly attached to the surface of the reinforcing bar, and the corroded regions identified by visual observation were directly marked on the film.

The cellophane film removed from the reinforcing bar was scanned and converted into a planar image. The marked corroded regions were then processed using Photoshop to remove the background and perform image binarization. Finally, the area of the corroded regions was quantitatively calculated from the binarized images using InnerView 2.0 (Innerview Co., Ltd., Seongnam-si, Gyeonggi-do, Republic of Korea) image analysis software. The corrosion area reported for each experimental condition was calculated as the average value obtained from the two specimens.

3. Experimental Results

3.1. Fresh Properties and Compressive Strength of Concrete

The slump and air content results, representing the fresh properties of concrete, are shown in Figure 5a, and the compressive strength results at 7 and 28 days are presented in Figure 5b. The slump and air content measurements confirmed that all mixtures satisfied the target slump of 180 ± 25 mm and target air content of $4.5 \pm 1.5\%$.

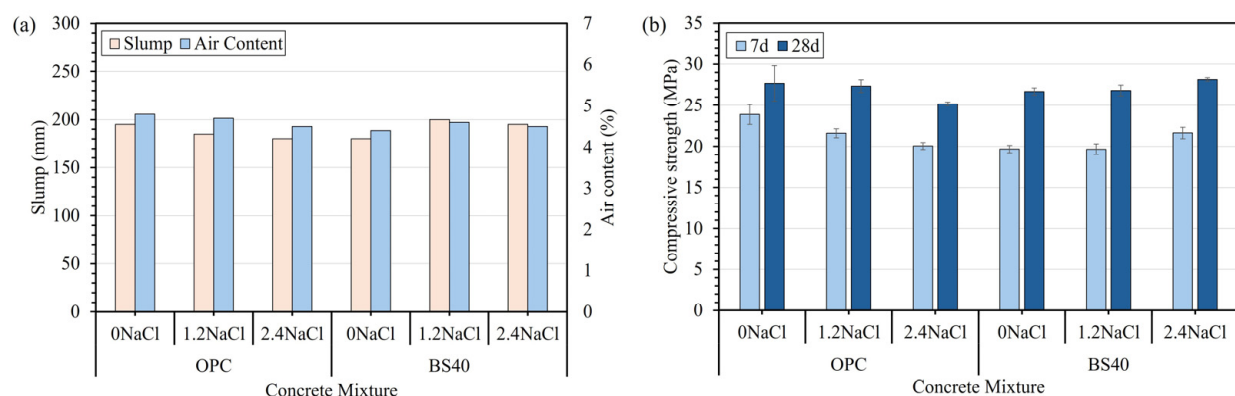


Figure 5. Fresh properties and compressive strength of concrete: (a) slump and air content and (b) compressive strength.

The compressive strength results showed that all mixtures exceeded the target strength of 24 MPa at 28 days. However, for the concrete in which OPC was partially replaced with GGBS, no significant reduction in compressive strength was observed with the incorporation of NaCl. In contrast, the concrete containing only OPC showed a slight decrease in both early-age and long-term compressive strength as the NaCl content increased.

3.2. Air Permeability Test Results

The air permeability test results are presented in Figure 6. At 28 days, some variation was observed among the mixtures; however, the air permeability coefficient of the uncoated specimens was $350.25\text{--}391.58 \times 10^{-19} \text{ m}^2$. In contrast, the value for the coated specimens was $3.62\text{--}4.05 \times 10^{-19} \text{ m}^2$, corresponding to a reduction of approximately 98.97% after coating application. These results indicate that the epoxy coating markedly restricted gas transport through the concrete surface and may effectively limit the oxygen supply required for reinforcing steel corrosion.

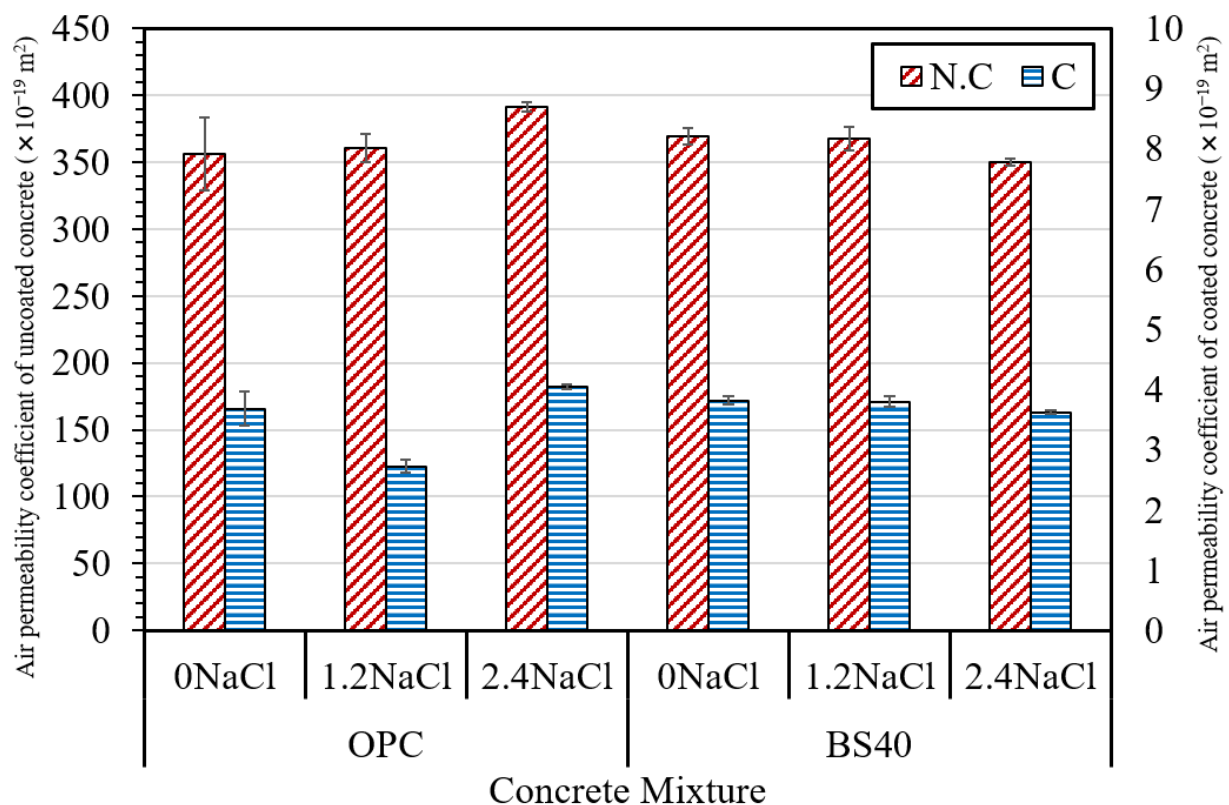


Figure 6. Air permeability coefficients of uncoated and coated concrete mixtures (N.C: non-coated; C: coated).

3.3. Half-Cell Potential Measurement Results

The half-cell potentials measured using the lead combined electrode were converted to equivalent potentials relative to the Cu/CuSO_4 reference electrode according to the conversion method presented in Table 4, and the results are shown in Figures 7 and 8. In the specimens without NaCl incorporation, both OPC and BS40 maintained half-cell potentials higher than -350 mV , regardless of whether the coating was applied. According to ASTM C876, these values do not correspond to a high probability of active corrosion. As will be discussed in the following section, no visible corrosion was observed on the reinforcing steel after the exposure period. Therefore, under the experimental conditions and within the monitoring period of this study, no clear evidence of reinforcing steel corrosion was identified in the specimens without internally incorporated chloride ions.

When NaCl corresponding to a chloride ion content of 1.2 kg/m^3 was incorporated, no pronounced decrease in half-cell potential was observed in the coated specimens of either OPC or BS40 throughout the monitoring period. In contrast, in the uncoated OPC specimens, the half-cell potentials of the two replicate specimens sharply decreased below -350 mV at 32 and 45 days, respectively, indicating a high probability of active corrosion according to ASTM C876. For BS40, only one of the two uncoated specimens exhibited a

decrease below -350 mV, which occurred at approximately 68 days. These results indicate that the pronounced negative shift in half-cell potential associated with an increased probability of corrosion occurred later in BS40 than in OPC under the investigated condition.

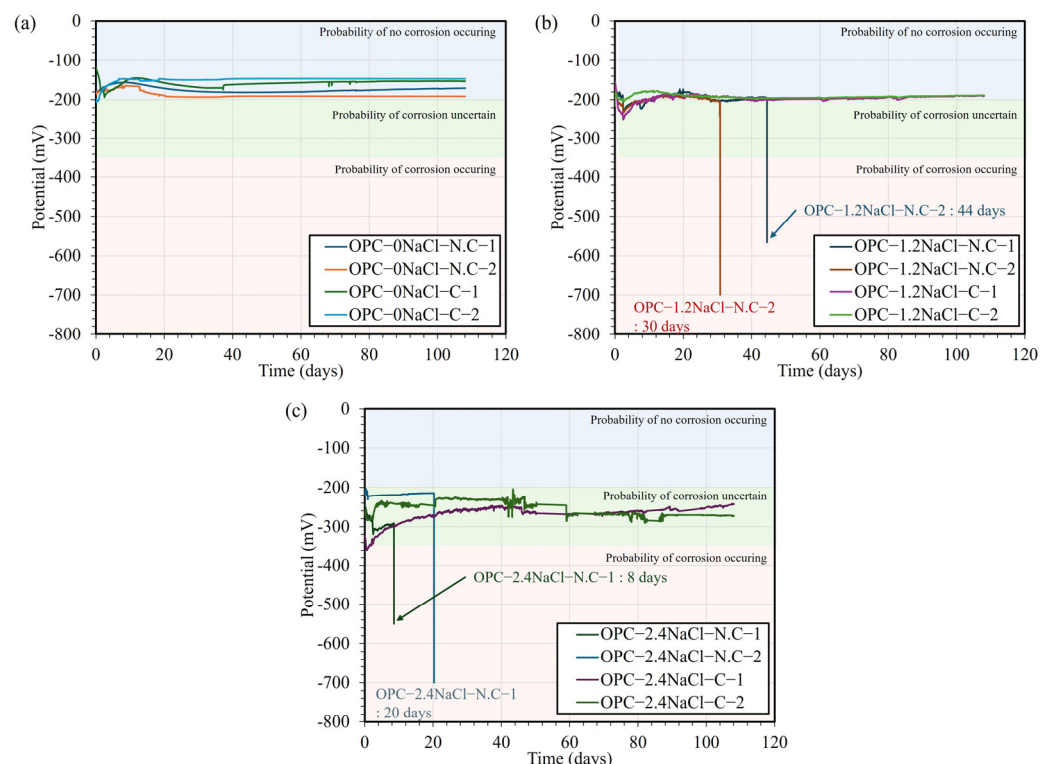


Figure 7. Half-cell potential measurement results: (a) OPC-0NaCl, (b) OPC-1.2NaCl, and (c) OPC-2.4NaCl.

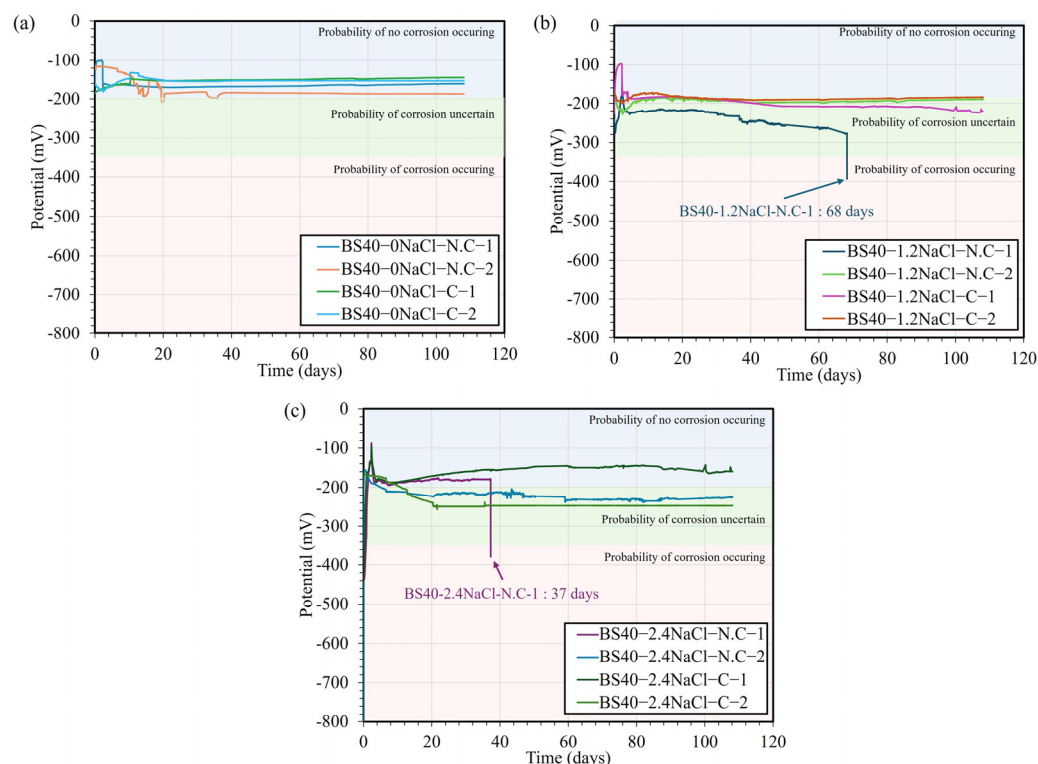


Figure 8. Half-cell potential measurement results: (a) BS40-0NaCl, (b) BS40-1.2NaCl, and (c) BS40-2.4NaCl.

For the OPC specimens containing 2.4 kg/m^3 of chloride ions, which were prepared to represent a relatively severe internally incorporated chloride condition, two of the four specimens exhibited sharp decreases in half-cell potential to below -350 mV at approximately 10 and 20 days, respectively. These measurements indicate that a high probability of active corrosion was present in these specimens before the coating was applied at 28 days. In contrast, no comparable sharp decrease in half-cell potential was observed in the remaining two specimens up to 28 days.

For the two specimens that did not exhibit an early sharp decrease in half-cell potential, the epoxy coating was applied at 28 days. Although their half-cell potentials remained above -350 mV , they were generally within the range of -350 to -200 mV , corresponding to an uncertain probability of corrosion according to ASTM C876. After coating application, the half-cell potential showed a slight decrease at approximately 46 days but did not fall below -350 mV during the subsequent monitoring period.

Notably, specimens prepared with the same mixture exhibited different electrochemical responses at early ages. This specimen-to-specimen variability may have been influenced by local differences in concrete quality around the reinforcing steel. In particular, bleeding during casting may have increased local porosity near the casting surface and altered the transport characteristics of the surrounding concrete [44]. Differences in compaction, steel–concrete interfacial conditions, or the initial surface condition of the reinforcing steel may also have contributed to the observed variability. However, because these factors were not directly quantified in the present study, their effects could not be conclusively determined. Further investigation is therefore required to clarify the origin of the specimen-to-specimen variability observed under these conditions.

In the case of BS40 containing 2.4 kg/m^3 of chloride ions, the half-cell potentials measured immediately after casting were generally higher than -200 mV , corresponding to a relatively low probability of corrosion according to ASTM C876. Among the uncoated specimens, only one specimen exhibited a pronounced decrease in half-cell potential associated with a higher probability of active corrosion at approximately 37 days, whereas no comparable decrease was observed in the coated specimens throughout the experimental period. These results suggest that the electrochemical response associated with corrosion activity tended to occur later in BS40 than in OPC under the conditions investigated.

Overall, the half-cell potential measurements showed that the pronounced negative shift in potential associated with an increased probability of reinforcing steel corrosion tended to occur later in the GGBS-containing concrete than in the OPC concrete. Previous studies have reported that GGBS-containing systems can exhibit enhanced chloride-binding capacity because of their chemical composition and hydration products, including the possible formation of chloride-bearing phases such as Friedel's salt [45–47]. Such mechanisms may reduce the availability of free chloride ions in the pore solution and may therefore contribute to the different electrochemical responses observed between OPC and BS40. However, free chloride concentration, chloride-binding capacity, Friedel's salt content, pore-solution chemistry, and concrete electrical resistivity were not directly measured in the present study. Accordingly, the relationship between the incorporation of GGBS and the observed half-cell potential behavior should be interpreted as a possible mechanism supported by previous studies rather than as a mechanism directly demonstrated by the present experimental results.

It should also be noted that half-cell potential measurements provide information regarding the probability and electrochemical tendency of reinforcement corrosion but do not directly quantify the corrosion rate. Therefore, the changes in half-cell potential observed in this study were interpreted primarily as indicators of corrosion probability and electrochemical activity rather than as direct evidence of the rate or extent of corrosion propagation.

Quantitative assessment of corrosion kinetics would require complementary techniques, such as linear polarization resistance or electrochemical impedance spectroscopy.

3.4. Corroded Area Measurement Results of Reinforcing Steel

After confirming the initiation of reinforcing steel corrosion through half-cell potential measurements, Figure 9 shows the corrosion morphologies of the extracted reinforcing bars, and Figure 10 presents the quantitative results of the corroded area determined by image binarization analysis. In the specimens without chloride ion incorporation, no corrosion was observed on the surface of the reinforcing steel, which is consistent with the half-cell potential measurement results. Meanwhile, in the specimens containing 1.2 kg/m³ of chloride ions, corrosion was clearly observed in the uncoated specimens, whereas corrosion was effectively suppressed in the coated specimens.

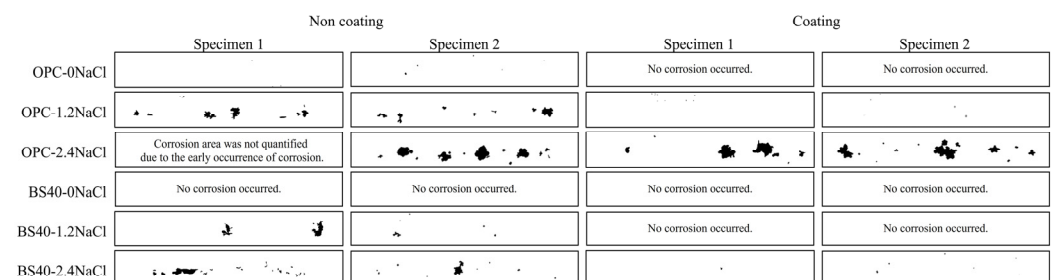


Figure 9. Corrosion morphology of the reinforcing steel.

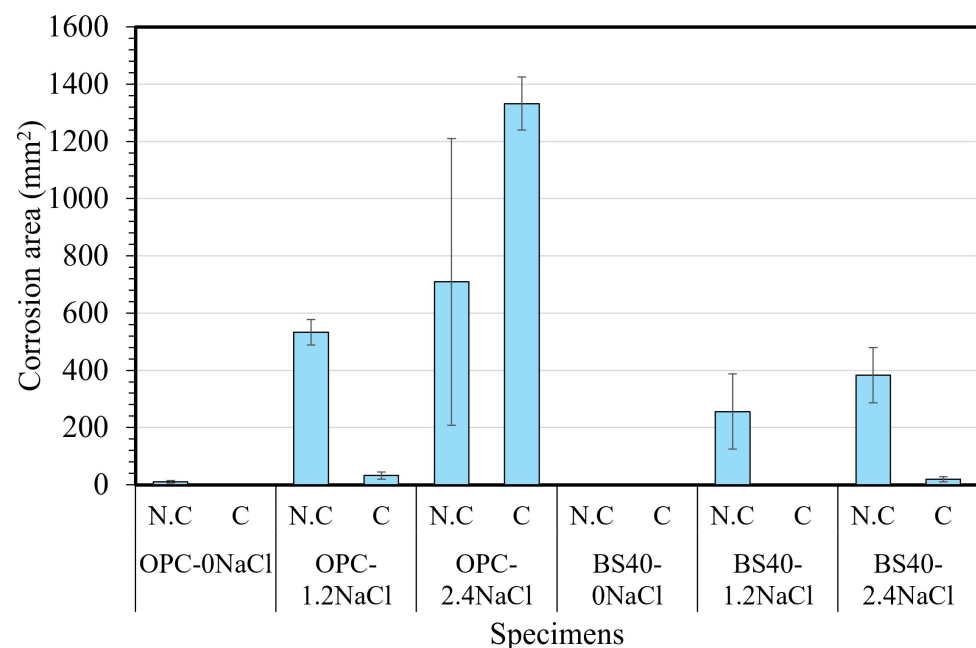


Figure 10. Quantitative analysis of the corroded area of reinforcing steel (N.C: non-coated; C: coated).

When 2.4 kg/m³ of chloride ions was incorporated, reinforcing steel corrosion was observed in all uncoated specimens. In contrast, among the coated specimens, almost no corrosion was observed in BS40, whereas corrosion occurred in OPC. This result can be explained by the half-cell potential behavior: in BS40, the potential was measured above −200 mV immediately after casting, indicating a very low probability of corrosion, whereas in OPC, the potential remained within the uncertain corrosion probability range of −350 to −200 mV from the early age until the end of the measurement period. This suggests that chloride-induced corrosion of reinforcing steel continues to progress in the OPC specimen.

The quantitative analysis of the corroded area showed that the OPC-2.4NaCl-coated specimen exhibited the largest corroded area, with a value of 1332.2 mm². This was followed by OPC-1.2NaCl without coating at 533.4 mm², BS40-2.4NaCl without coating at 383.6 mm², and BS40-1.2NaCl without coating at 225.6 mm². In all other specimens, the corroded area was less than 10 mm², indicating a very low level of corrosion.

In general, when ground granulated blast-furnace slag is incorporated, its chloride binding capacity can increase with increasing replacement ratio through the formation of Friedel's salt. In this study, BS40 also showed a tendency to delay the initiation of reinforcing steel corrosion owing to the chloride binding effect associated with Friedel's salt formation. However, when the chloride ion content was excessive, reinforcing steel corrosion could still be initiated by free chloride ions, even though a certain amount of chloride ions was bound in the form of Friedel's salt. Nevertheless, the application of a coating can effectively reduce the diffusion of oxygen and moisture, thereby suppressing the propagation of reinforcing steel corrosion. However, in the case of concrete containing only OPC, when the chloride ion content exceeds the threshold level, the probability of corrosion becomes very high. Therefore, it is considered necessary to limit the amount of chloride ions incorporated into OPC-based concrete.

Nevertheless, it should be noted that the corrosion assessment in the present study relied primarily on half-cell potential measurements, which indicate the probability of corrosion occurrence but do not directly quantify the corrosion rate. Therefore, future studies should employ complementary electrochemical techniques, such as linear polarization resistance or electrochemical impedance spectroscopy, to quantitatively evaluate the corrosion rate and further clarify the corrosion behavior of reinforcing steel.

4. Discussion

The present study aimed to evaluate the effects of surface coating and GGBS incorporation on the corrosion behavior of reinforcing steel in concrete containing internally admixed chloride ions. The experimental results showed that the coated specimens generally exhibited less pronounced decreases in half-cell potential than the corresponding uncoated specimens under the investigated conditions. In addition, the average air permeability coefficient decreased by approximately 98.97% after coating application, indicating that the coating formed an effective barrier to pressure-driven gas transport through the concrete surface. This result is consistent with a previous study reporting a marked reduction in the gas permeability of surface-coated concrete [48].

Sakai [49] reported a strong relationship between air permeability and gas diffusivity in cementitious materials, including oxygen diffusivity, and demonstrated that oxygen diffusivity can be estimated from measured air permeability coefficients. Although permeability and diffusion are driven by different mechanisms, namely pressure and concentration gradients, respectively, both are strongly influenced by the connectivity and size of the pore network. Accordingly, the pronounced reduction in air permeability observed after coating application suggests that the epoxy coating may also have restricted the transport pathways available for oxygen ingress. Such a change in gas transport characteristics could potentially reduce oxygen availability at the steel surface and thereby influence the cathodic oxygen-reduction reaction. However, oxygen diffusivity and moisture transport were not directly measured in the present study; therefore, their contributions to the observed corrosion behavior cannot be conclusively determined from the air permeability results alone.

The corrosion-related electrochemical response was also influenced by the binder composition. Compared with the corresponding OPC specimens, BS40 generally exhibited a later pronounced negative shift in half-cell potential. This behavior may be associated with

the enhanced chloride-binding capacity of the GGBS-containing binder. Previous studies have reported that increasing the GGBS replacement ratio can enhance chloride binding because calcium- and aluminum-bearing phases promote the formation of chloride-bearing AFm phases, including Friedel's salt [30,50]. In addition, GGBS can contribute to pore refinement and reduced chloride mobility. These mechanisms may decrease the amount of free chloride available at the steel–concrete interface and thereby contribute to the different electrochemical behavior observed in BS40. However, free chloride concentration, chloride-binding capacity, Friedel's salt content, pore-solution chemistry, and concrete electrical resistivity were not directly measured in the present study. Therefore, the improved electrochemical behavior observed in BS40 cannot be conclusively attributed to chloride binding or Friedel's salt formation based on the present experimental results alone, and these mechanisms should instead be regarded as possible explanations supported by previous studies.

At the higher internally incorporated chloride content of 2.4 kg/m^3 , BS40 specimens also exhibited electrochemical responses associated with an increased probability of corrosion, although these changes generally occurred later than those in the corresponding OPC specimens. This finding suggests that the beneficial influence associated with GGBS incorporation may become less pronounced as the internally incorporated chloride content increases. Similarly, although the coated specimens generally exhibited less pronounced changes in half-cell potential, a relatively large corroded area was observed in the coated OPC specimen containing 2.4 kg/m^3 . This result indicates that surface coating alone may not be sufficient to prevent corrosion-related damage when a relatively high amount of chloride is already present within the concrete. Internally admixed chloride ions are distributed within the concrete from the time of casting, and the local electrochemical response may also be affected by the heterogeneous characteristics of the steel–concrete interface [27,28]. Therefore, surface coating may modify subsequent transport conditions at the concrete surface but cannot remove internally incorporated chlorides or directly restore an already destabilized passive condition.

The chloride content of 1.2 kg/m^3 used in the present study should not be interpreted as a universally applicable critical chloride threshold. Previous reviews have demonstrated that the critical chloride content varies widely depending on binder composition and content, water-to-binder ratio, pore-solution alkalinity, chloride-binding capacity, steel surface condition, steel–concrete interface, exposure environment, and the criterion used to define corrosion initiation [27,51]. In this study, 1.2 kg/m^3 was adopted as an experimental reference level based on the chloride limits specified in existing standards, whereas 2.4 kg/m^3 was selected as a severe chloride condition corresponding to twice the reference level. Therefore, the corrosion behavior observed at these chloride contents should be interpreted within the context of the specific materials and experimental conditions employed in this study rather than as evidence of a universal chloride threshold.

The present investigation was limited to a GGBS replacement ratio of 40% and a fixed binder content. Consequently, the results are insufficient to establish a general critical chloride content for GGBS concrete. Further studies should systematically investigate different GGBS replacement ratios, total binder contents, water-to-binder ratios, and internally incorporated chloride levels. Direct measurements of chloride speciation, hydration products, pore-solution chemistry, and concrete electrical resistivity are also required to clarify the mechanisms responsible for the different electrochemical responses observed between OPC and GGBS concretes. In addition, complementary electrochemical techniques, such as linear polarization resistance and electrochemical impedance spectroscopy, should be employed to quantitatively evaluate the corrosion rate.

5. Conclusions

In this study, the effects of binder type, chloride ion incorporation level, and surface coating on the initiation and propagation of reinforcing steel corrosion were experimentally evaluated using 24 MPa-class normal-strength concrete. Half-cell potential measurements and quantitative analysis of corroded areas were conducted to assess the corrosion behavior of reinforcing steel. Based on the experimental results, the following conclusions can be drawn:

- In the specimens without chloride ion incorporation, no significant decrease in half-cell potential was observed, and no visible corrosion was detected on the reinforcing steel surface, regardless of the binder type or coating condition. These results indicate that no clear evidence of reinforcing steel corrosion was observed during the experimental period under the investigated conditions.
- As the chloride ion content increased, the probability of reinforcing steel corrosion increased. In the uncoated specimens containing chloride ions, the half-cell potential decreased below the corrosion threshold of -350 mV, and visible corrosion was confirmed on the reinforcing steel surface. These results suggest that internally incorporated chloride ions increased the likelihood of passive-film destabilization and reinforcement corrosion under the investigated conditions.
- The incorporation of GGBS tended to delay the initiation of reinforcing steel corrosion compared with OPC concrete under the conditions investigated in this study. This behavior may be associated with the enhanced chloride-binding capacity of GGBS-containing systems, which can reduce the concentration of free chloride ions in the pore solution through chloride binding, including the possible formation of Friedel's salt. Therefore, the use of GGBS may contribute to reducing the corrosion risk associated with internally incorporated chloride ions.
- The application of epoxy coating was associated with a smaller decrease in half-cell potential and a smaller corroded area of reinforcing steel under the investigated conditions. These results suggest that restricting the transport of oxygen and moisture through the surface coating may contribute to delaying or reducing the progression of reinforcing steel corrosion, even when chloride ions are present in concrete.
- However, in the OPC specimen containing 2.4 kg/m^3 of chloride ions, a relatively large corroded area was observed even under the coated condition. This observation suggests that at relatively high internally incorporated chloride contents, corrosion may already have initiated before coating application or may continue because of the availability of free chloride ions. Therefore, appropriate control of internally incorporated chloride content remains important, particularly for OPC-based concrete.
- A limitation of the present study is that the corrosion assessment was primarily based on half-cell potential measurements; therefore, the corrosion rate was not directly quantified. Future studies should employ complementary electrochemical techniques, such as linear polarization resistance and electrochemical impedance spectroscopy, to enable a more quantitative evaluation of reinforcing steel corrosion.

Overall, the results indicate that, within the experimental conditions considered in this study, the corrosion behavior of reinforced concrete containing internally incorporated chloride ions may be influenced not only by the total chloride content but also by binder type, chloride-binding capacity, and oxygen and moisture transport conditions. These findings may provide useful fundamental data for establishing rational chloride ion criteria for cement and concrete, particularly in relation to the increased use of alternative fuels in the cement industry.

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Abbreviations

The following abbreviations are used in this manuscript:

OPC	Ordinary Portland cement
GGBS	Ground granulated blast-furnace slag
C	Coating
N.C	Non coating
SCMs	Supplementary Cementitious Materials
W/B	Water-to-binder ratio
S/a	Sand percentage

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