



Corrosion of rebar in concrete under cyclic freeze–thaw and Chloride salt action



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HIGHLIGHTS

- The coupled freeze–thaw and Chloride salt environments were considered.
- An ordinary concrete and a ternary-binder concrete were tested.
- Both the open circuit potential and Tafel potentiodynamic polarization measurements were conducted.
- Corrosion of rebar was depressed due to temperature effect and ice obstruction.

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ABSTRACT

We studied the coupled effects of freeze–thaw (F–T) cycling and chloride on corrosion of rebar in concrete. An ordinary concrete and a ternary-binder concrete were immersed in 3.5 wt.% NaCl solution and endured up to 200 F–T cycles. We found: (1) the risk of corrosion of steel reinforcement in concrete remained in the “passive region”, even with increasing F–T cycling, although serious spalling occurred for all concrete specimens; (2) factors that reduce rebar corrosion include lower temperatures, non-wetting phase percolation which blocks harmful chloride penetration, and insufficient oxygen supply; and (3) blends do not seem to improve the resistance to reinforcement corrosion.

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1. Introduction

Corrosion of rebar in concrete is crucial to the durability of reinforced concrete structure, especially in an aggressive environment. Investigations of the corrosion of rebar in concrete structures are being intensively pursued, because such corrosion can cause serious damage to concrete, and eventually failure of the structure. A large number of laboratory studies have been conducted, most of which focus on a single factor that impacts the corrosion process such as penetration of chloride ions, carbonation of concrete, or loading levels [1–7]. There is also a rapidly increasing amount of research into corrosion of reinforcement in concrete by coupled factors, since reinforced structures generally experience complex environmental and mechanical loadings [8–15], but many combined aspects have not yet been examined in sufficient detail.

Generally, the high alkalinity of ordinary concrete pore solution can chemically protect rebar against corrosion. A passive layer of a

few nanometers thick builds up progressively as concrete is cast [16,17]. Therefore, the rebar in well cast and cured reinforced concrete structures usually has very low risk of corrosion, or at least shows a prolonged initiation period before corrosion. However, in aggressive environments, the alkalinity of pore solution decreases, weakening the protection offered by the passive layer. Pitting corrosion may initiate at some places on the rebar surface where the passive layer has been weakened. As the corrosion proceeds, rust appears. Rust has a significantly greater volume than steel, and it has been reported to have an apparent modulus of around 100 MPa [18], which can induce cracks in concrete cover [19–21]. Previous studies indicated that the deicing salts can substantially increase the corrosion risks of rebar in concrete [15,22,23].

Like most corrosion processes, corrosion of rebar in concrete is an electrochemical process. An anodic area where an oxidation reaction occurs ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$), a cathodic area where a reduction reaction occurs ($1/2\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^{2-}$) and a conducting medium for the transportation of ions between anode and cathode are all required for the electrochemical reactions of

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the corrosion process to proceed [9,24]. The electrochemical nature of corrosion means that electrochemical techniques can be used to monitor and/or assess the corrosion behavior of rebar in concrete. Those techniques include half-cell potential measurement, surface potential measurement, linear polarization resistance measurement, Tafel potentiodynamic polarization (TPP) measurement, galvanostatic pulse transient method, and electrochemical impedance spectroscopy [25–27]. Half-cell potential measurements are one of the most widely used techniques to inspect the state of rebar in concrete. By measuring the electrical potential of the rebar relative to a stable reference half-cell on the outer surface of the concrete, (i.e. open-circuit potential (OCP) measurement), this technique can diagnose the corrosion risk of reinforced concrete structures. It is noteworthy that many factors, such as polarization by limited diffusion of oxygen, concrete porosity and the presence of highly resistive layers [25], may lead to erroneous diagnoses, thus the OCP values alone are not sufficient as corrosion criteria. In addition, the OCP values provide little quantitative information regarding the corrosion rate [24]. The TPP measurement is also widely used to diagnose the corrosion behavior of rebar embedded in concrete [2,14]. Erroneous estimation of the Tafel slopes may occur either from selection of the region of the curve to analyze, or because the current–potential characteristics may not conform to the Butler–Volmer equation [28]. However, compared with the other methods, the Tafel Extrapolation method offers several significant advantages: it is rapid and easy to operate, reads the corrosion current directly, provides sufficiently accurate results, can be used to monitor the corrosion rate of a system continuously, and covers the overall effect of a number of electrochemical parameters [25]. In the present study, OCP and TPP measurements were employed as the two main methods to monitor the corrosion of rebar in concrete.

Practically, great efforts are made to improve the properties of cover concrete to prevent environmental attacks. Freeze–thaw (F–T) action can be one of the most aggressive attacks on concrete, because cyclic F–T attack can cause serious internal cracking and superficial spalling [29]. Consequentially, concrete loses its resistance to mechanical loading (e.g., decreases occur in dynamic elastic modulus and compressive (split) strength) and penetration of harmful ions (e.g. increases in gas and water permeability, and Cl^- diffusion coefficient). In addition, the bond strength between concrete and rebar is diminished by F–T loading [30], and the degradation of performance of reinforced concrete can be accelerated by persistent mechanical and salt solution loading [31–33]. Alternatively were made the attempts that use the inhibited deicing salts (e.g., chloride-based salts) to decrease the corrosion risks of rebar in concrete under coupled environmental loadings [15,34,35]. Despite reducing corrosion risks of rebar in concrete, the inhibited deicing salts are suspected to impose detrimental effects on the microstructure of cement hydrats in concrete (such as, leaching of calcium hydroxide and chemical alterations) [34,36]. The pronounced damages to both the concrete and the embedded rebar were frequently observed when deicing salts were used on reinforced concrete structures to thaw ice in winter.

Despite an ongoing awareness on deicing damage to rebar in concrete, the joint action of cyclic F–T and sodium chloride solution on the relative degree of damage to the concrete and the embedded rebar is not thoroughly documented. A concrete made from ordinary Portland cement (OPC) and a concrete containing ternary binders (OPC plus two types of slags) were prepared to undertake a comparative study. Both OCP and TPP measurements were employed to evaluate the electrochemical properties of the rebar under a number of F–T cycles. A temperature-governed reaction mechanism and an ice percolation related mechanism were discussed to explain the passivation of rebars in both types of concrete specimens.

2. Experiments and materials

2.1. Materials and mixture

The binders used for concrete were ASTM Type I Portland cement (refer to ASTM C150–00, “Standard Specification for Portland Cement”), ground granulated blast furnace slag (GGBFS) and ground granulated blast steel furnace slag (GGBSFS). The chemical composition and physical properties of the binders used are presented in Table 1. The GGBFS has a much larger value of specific surface area (SSA) than those of the cement and the GGBSFS. Two types of concrete were designed in this study (type R and type S), see Table 2. In type R concrete, ordinary Portland cement was the only binder. In type S concrete, 30% mass cement was replaced by supplemental materials (GGBFS and GGBSFS with mass ratio of 2:1). Qualified fine aggregate and coarse aggregate were used to cast the concrete. The modulus of fineness of the fine aggregate was 2.8, with the soil content less than 1%, and the coarse aggregate was continuously graded with a size range of 5–20 mm. The ratio of coarse aggregate: fine aggregate: binder is 3.12: 1.84: 1. A water-to-binder (W/B) ratio of 0.39 was adopted in this study. A water reducer (naphthalene series) with mass ratio of 1% was used to improve the rheology of fresh concrete, see Table 2. The used rebar is an ordinary ribbed steel according to the Chinese standard GB 1499.2–2007 (“Steel for the reinforcement of concrete– Part 2: Hot rolled ribbed bars”).

2.2. Sample preparation

Steel rebars of diameter 10 mm were cut into rods, 360 mm long. The rods were polished with 400# grit SiC emery paper, and ethanol and acetone treatments were used to degrease their surfaces. One end of each steel rod was welded to a copper wire, and the weld and surrounding area were covered with a layer of epoxy resin, partially to protect the weld, and also to control the exposed area of steel. Each steel rod was placed at the bottom of a prism mould with dimensions of $100 \times 100 \times 400 \text{ mm}^3$.

After an appropriate mixing procedure, the two types of fresh concrete were cast into the prism moulds containing rebar. The distance between the outside of the steel and the bottom of the mould was controlled to be 20 mm. The concrete prisms were placed in a room at 20 °C for primary curing. After 24 h curing, the hardened concrete specimens were demoulded. Two groups of concrete specimens were designed in this study. The concrete specimens in the first group under standard curing scheme (i.e., in a chamber with >90% humidity) were ready for the strength tests. The concrete specimens in the second group under salt-rich curing environment (i.e., 3.5 wt.% NaCl solution) were ready for F–T tests. After 28 days, strength measurements (compressive and split strengths) were conducted on the reference concretes, according to the Chinese standard GB/T 50081–2002 (“Standard for Test Method of Mechanical Properties on Ordinary Concrete”). The compressive strengths of R and S concretes were 56 MPa and 52 MPa, and the split strengths were 4.8 MPa and 4.3 MPa, respectively. The OCP and TPP measurements were conducted on the concrete specimens cured in NaCl solution, which were then placed into a refrigerating chamber for F–T tests. After every 50 F–T cycles, the OCP and TPP tests were performed on each type of concrete. For each test, two specimens were measured to verify the reproducibility.

2.3. F–T course

Cyclic F–T loading of samples immersed in NaCl solution was performed on the two types of concrete specimens—see Fig. 1 for an illustration of the experimental setup. The F–T course was designed in reference to, but is not the same as, ASTM C 666 (“Standard test method for resistance of concrete to rapid freezing and thawing”) and RILEM proposed Cube test. The temperature range was 15 to –30 °C,

Table 1

Mass compositions and physical properties of cement, GGBFS and GGBSFS (LOI: loss of ignition, SSA: specific surface area).

Chemical composition	Cement	GGBFS	GGBSFS
SiO_2 (%)	22.02	32.86	17.36
Al_2O_3 (%)	4.00	16.38	6.98
Fe_2O_3 (%)	3.48	0.97	18.96
CaO (%)	62.12	36.31	40.33
MgO (%)	2.58	9.37	5.90
SO_3 (%)	2.72	9.37	0.59
$\text{Na}_2\text{O}(\text{eq})$ (%)	0.53	–	–
CaO (free) (%)	0.87	0.018	0.55
Cl (%)	0.01	0.02	0.024
LOI (%)	1.75	0.86	5.00
SSA (m^2/kg)	343	449	332
Density (g/ml)	3.10	2.78	–

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