Effects of w/b ratio, fly ash, and chloride content on corrosion of reinforcing steel

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Abstract. To predict the corrosion of reinforcing steel, the electrochemical properties of reinforcing steel with different concrete mix proportions and chloride content were studied. The water to binder ratio of concrete was varied (0.45 and 0.60). Coal fly ash was used to replace OPC (0 and 30% by weight of the total binder). The initial chloride was 0, 2, and 4% by weight of concrete. Potentiodynamic polarization testing was conducted by controlling the moisture of specimens. The Tafel slope, corrosion potential, and corrosion rate were analyzed from the testing results. Results show that chloride content significantly affects the electrochemical properties of reinforcing steel. The anodic Tafel slope decreased as chloride content increased. The cathodic Tafel slope increased when the water to binder ratio decreased, or when the fly ash content increased due to a denser concrete pore structure, limiting oxygen diffusion. Results from this study can be used to simulate the corrosion of reinforcing steel and predict the service life of reinforced concrete structures. Also, the electrochemical compatibility between existing and repaired sections can be evaluated to ensure the durability of repaired RC structures.

1. Introduction
The corrosion of reinforcing steel (RC) is a major problem, deteriorating reinforced concrete structures worldwide. To ensure the safety of an RC structure throughout its service life, performance prediction must be accurately performed. For the corrosion of reinforcing steel, the deterioration mechanism is normally classified into 4 stages: corrosion initiation, corrosion propagation, corrosion acceleration, and deterioration. In each stage, different prediction models are required. For example, corrosion initiation due to chloride attack or carbonation can be predicted based on Fick’s 2nd diffusion law. After corrosion has been initiated, the time to corrosion cracking can be predicted based on the corrosion rate of reinforcing steel and structural conditions such as concrete strength or the location of the reinforcing steel. Many researchers studied the corrosion rate of reinforcing steel [1]. It is well known that the corrosion rate depends on concrete properties such as chloride content, pH, moisture, oxygen, temperature, electrical resistivity, etc. In previous studies, the corrosion rate was measured by corrosion mass loss, embedded corrosion sensors, linear polarization, half-cell potential, or electrical resistivity. Equations to predict the corrosion rate has been proposed.
The corrosion rate of reinforcing steel is basically an electrochemical reaction. To understand and predict the corrosion rate correctly, a study of the electrochemical properties of reinforcing steel in concrete is necessary. Initially, reinforcing steel is protected from corrosion because of the high alkalinity of concrete, forming a passive film on the steel surface. However, the presence of chloride or a decrease in pH due to carbonation destroys the passive film. The electrochemical reaction of steel corrosion consists of anodic and cathodic reactions as shown in Equations (1) and (2), respectively. The Anodic reaction occurs at a location that the passive film of reinforcing steel was destroyed, and steel gradually dissolves in solution and releases electrons. Steel at an anodic area decreases its cross-sectional area. The area of a cathodic reaction is a location where the released electrons from the anode are consumed by oxygen and water. Then, it will generates rusts and cracks the concrete surface.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

Figure 1 shows an Evans diagram that is widely used to study the corrosion of metals. In this figure, the corrosion potential and current of steel at different stages of anodic and cathodic reactions are plotted. The anodic and cathodic lines are fitted from the most linear part, leading to the open circuit potential of the Evans diagram, as shown in figure 2. Equilibrium of anodic and cathodic reactions occurs at the intersection of the anodic and cathodic lines. The corrosion current of reinforcing steel can be determined. From the linear fitted anodic and cathodic lines, 4 electrochemical parameters can be extracted to explain the electrochemical corrosion of reinforcing steel, as shown in figure 3. Those are the anodic Tafel slope ($\beta_a$), cathodic Tafel slope ($\beta_c$), anodic equilibrium potential ($E_{eq}^a$), and cathodic equilibrium potential ($E_{eq}^c$).

In this study, the electrochemical properties of reinforcing steel in different concrete mix proportions and chloride content were studied using the potentiodynamic polarization test. The effects of the anodic and cathodic Tafel slopes on the corrosion rate are shown in figure 4. A smaller absolute value of the anodic or cathodic Tafel slope increases the corrosion rate of reinforcing steel.
2. Methodology
Small cubic reinforced concrete specimens were prepared with different concrete mix proportions and chloride content. The electrochemical properties of reinforcing steel were measured by potentiodynamic polarization measurements.

2.1. Materials
Ordinary Portland Cement (OPC) type 1 (according to ASTM C150) and coal fly ash type 2b (according to TIS2135) were used as a binder. Natural silica sand and limestone gravel were used as the aggregate. Tap water was used as the mixing water. Food grade sodium chloride was mixed in the
mixing water for the initial chloride contamination in concrete. Deformed bar grade SD40 (according to TIS24) with a diameter of 20 mm was used as reinforcing steel. Before the casting process, both ends of the reinforcing steel were coated by an epoxy paint and degreased by acetone. The middle portion of steel, 8 cm in length and 50 cm² of surface area, was exposed for testing.

Concrete mix proportions were varied for water bind ratio, fly ash content, and chloride content. The water to binder ratio of concrete was varied (0.45 and 0.60). OPC was partially replaced by coal fly ash at 0 and 30% by weight of the total binder. Chloride was initially mixed in the mixing water (0, 2 and 4% by weight of concrete). The total aggregate content was fixed in all specimens.

2.2. Specimen preparation
Cubic reinforced concrete specimens were prepared with a size of 10x10x10 cm³. The covering depth of reinforcing steel was fixed at 2 cm, as shown in figure 5. After the casting process, specimens were cured by plastic wrapping for 28 days before testing.

![Figure 5. Specimen shape (unit: mm).](image)

2.3. Testing
In this study, potentiodynamic polarization testing was conducted. Reinforcing steel acted as the working electrode and was connected to a potentiostat by conductive copper tape. Stainless steel grade 304 was used as the counter electrode and placed on the top surface of the concrete. The reference electrode was saturated Cu/CuSO₄, placed on top of the middle point of the reinforcing steel. The conductive gel was applied between the stainless steel and concrete surfaces to ensure good electrical connectivity. Figure 6 shows the testing configuration.

![Figure 6. Testing configuration](image)

First, the open circuit potential (OCP) was determined for 150 seconds. Then, a potential was applied to the reinforcing steel with a range of ±120 mV from the OCP. The potential scan rate was 0.1 mV/s. Linear fitting was conducted to extract the anodic and cathodic lines from the raw data. The linear line from ±20 mV to ± 130 mV from the OCP was selected. The anodic and cathodic Tafel slopes were determined, as shown in figures 2 and 3.
3. Results and discussion

Results obtained from the potentiodynamic polarization test are shown in figures 7 to 12. The Evans diagrams (potential vs. log of corrosion current density) are shown. The effects of the initial chloride content were clearly observed as the potential of the reinforcing steel shifted to a more negative value when the chloride content increased. This is because the passive film was destroyed at a higher chloride content. For fly ash concrete, the potential of reinforcing steel was slightly lower than OPC concrete. This is due to the pozzolanic reaction of fly ash, decreasing the pH of fly ash concrete. As a result, the passive film of steel in fly ash concrete is slightly weaker than that in OPC concrete. Similarly, the potential of reinforcing steel in 0.60 w/b ratio concrete was lower than for the 0.45 w/b ratio concrete. This is because a higher amount of OPC was used for the low w/b ratio. As a result, the pH of low w/b concrete is higher than that of high w/b concrete. The passive film of steel in low w/b concrete is stronger.

Figure 13 shows the Tafel slopes of anodic and cathodic lines extracted from the Evans diagram. A smaller absolute value of anodic or cathodic Tafel slope increases the corrosion rate of reinforcing steel. The anodic Tafel slope decreased when the chloride content increased because the passive film was destroyed. Then, electrons were easily released. However, the chloride content increased the absolute value of the cathodic Tafel slope, which may reduce the corrosion rate. This is because chloride is known for moisture attraction. The saturation degree of concrete pores is higher and oxygen diffusion is limited with high chloride content [2, 3].

The anodic Tafel slope of OPC concrete was higher than that of FA concrete because of the lower pH of fly ash concrete. In contrast, the absolute cathodic Tafel slope of FA concrete was higher than OPC concrete because FA concrete is known to have a denser pore structure.

Figure 7. Effects of initial chloride content on w/b 0.45 OPC concrete. Figure 8. Effects of initial chloride content on w/b 0.45 FA30% concrete.
Figure 9. Effects of binder type on w/b0.45 and 0% chloride content.

Figure 10. Effects of binder type on w/b0.45 and 4% chloride content.

Figure 11. Effects of w/b on OPC concrete with 0% chloride content.

Figure 12. Effects of w/b on OPC concrete with 4% chloride content.

Figure 13. Effects of binder type and chloride content on Tafel slope.
4. Conclusions
Electrochemical properties of reinforcing steel were significantly affected by the concrete mix proportion and presence of chloride. The chloride content and fly ash decreased the potential of steel and the anodic Tafel slope but increased the cathodic Tafel slope. Because the corrosion rate is affected by both the anodic and cathodic Tafel slopes, it is difficult to predict the corrosion rate. The corrosion rate also depends on the equilibrium potential as well as the time dependence of the parameters. A prediction model of electrochemical corrosion of reinforcing steel is in progress. Results from this study can be used to simulate the corrosion of reinforcing steel and predict the service life of reinforced concrete structures. Also, electrochemical compatibility between existing and repaired sections can be evaluated to ensure the durability of the repaired RC structures.

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