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Rebar corrosion due to chlorides in synergy with sodium, potassium, and magnesium



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HIGHLIGHTS

• Galvanostatic pulse technique (GPT) is useful for assessing early stage rebar corrosion.

• Effects of chloride attack on rebars by assessment of corrosion related parameters is presented.

• The influence of cations in the corrosion process is discussed.

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ABSTRACT

The ability of steel reinforced concrete to withstand long service life is ensured by the strong binding between the concrete and the rebar. Although rebar corrosion deterioration in the presence of chlorides is well known, it is important to note that these anions are never present in isolation, *i.e.*, other cations are also present within the exposed environment. Consequently, a study was conducted to investigate the rebar deterioration due to chlorides in the presence of different cations. A well-controlled laboratory experiment for assessing the corrosivity of sodium chloride, potassium chloride and magnesium chloride was conducted. The galvanostatic pulse technique was used to investigate the concrete-steel interfacial structure, which was modelled after a modified Randles circuit. Analysis revealed influences of the associated cations during the rebar corrosion process. A normalisation approach was used to compare chloride attacks on the rebar due to different salt solutions. Results suggest that chloride attacks in the presence of sodium cations are relatively corrosive.

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1. Introduction

The versatility and durability as a construction material enables steel reinforced concrete to be used extensively. The durability of reinforced concrete significantly depends on the surrounding environmental exposure conditions [1]. Hence, it is important to understand concrete as a corrosive environment. Although concrete is porous, the embedded steel is to some extent protected from the corrosion through the formation of protective layers [1–3], formed due to oxidation of the rebars, which can avoid further rebar corrosion provided it is fully established and maintained. However, once exposed to a chlorinated environment, deterioration of the structures can continue [4].

Although chloride ions are mainly responsible for accelerated deterioration of rebars [4], the role of cations is seldom addressed

* Corresponding author. *E-mail address:* krishneel.sharma@uon.edu.au (K.K. Sharma). within the environment. Cations also get adsorbed in the concrete. Some studies [5,6] have reported that diffusion of chloride ions must be accompanied by diffusion of cations, although the cations mostly diffuse at a slower rate compared to anions, which eventually may slow down the diffusion rate of anions. De Weerdt et al. [7] highlighted that cations have important role regarding the chloride binding. This binding is further aggregated when cations are associated with large number of chlorides (e.g., MgCl₂ and CaCl₂).

1.1. The concrete-steel interface structure

The interface between concrete and steel can be described by the electrical double layer (EDL) phenomenology. Randles type circuit is useful in modelling the structure of the concrete/steel interface. This is characterised by the combined polarisation resistance (R_p) and the diffusion resistance (R_D) in parallel with a non-ideal double layer capacitance (C_{dl}) , which is in series with the concrete (Ohmic) resistance (R_Ω) [8–12] as shown in Fig. 1.









Fig. 1. Randles type circuit to model the concrete/steel interfacial structure.

The corrosion properties at the concrete/steel interface can be analysed using short galvanostatic pulse method [8–13]. It has been shown that the application of a small magnitude of current pulse (<100 μ C/cm²) eliminates the diffusion effects in the system [8,9,14,15], allowing the system to be analysed using the equivalent electrical circuit in Fig. 1 without consideration of R_D .

The potential time response, upon an application of a small duration (usually 1 s) current stimuli, can be modelled using the following equations for charging (Eq. (1)) and discharging (Eq. (2)) conditions.

$$\Delta E(t) = I_{app} R_{\Omega} + I_{app} R_{p} \left[1 - \exp\left(\frac{-t}{R_{p} C_{dl}}\right)^{\beta} \right]$$
(1)

$$\Delta E(t) = I_{app} R_p \left[\exp\left(\frac{-t}{R_p C_{dl}}\right)^{\beta} \right]$$
(2)

where, $\Delta E(t)$ is the potential-time response (V), I_{app} is the applied current (A), β is the stretched exponential factor to account for the non-ideality in C_{dl} . In this manner, the corrosion related parameters (R_p , C_{dl} , and β) can be determined using curve fitting techniques.

The present study is designed to provide an understanding on the influences of cations during rebar corrosion. This was achieved through analysis of the corrosion related parameters determined using the short galvanostatic pulse method. A normalisation approach was used to compare chloride attacks amongst the different salt solutions, enabling conclusions to be drawn more definitely on the role of different cations.

2. Experimental design

2.1. Materials and methods

Five different concentrations (0.01 M, 0.03 M, 0.06 M, 0.1 M and 0.15 M) of NaCl, KCl, and MgCl₂ solution were prepared. The rebar used in this study, a deformed Grade 300 rebar ($\phi = 10$ mm), was acquired from a local company. The concrete mortar specimens (total of 45 and a control) were submerged in the salt solution of different concentrations as noted above. Further details on the experiment are given in the respective sections below.

2.2. Preparation of concrete mortar specimens

The sand used in this study was locally acquired and sorted into fine (0.5-0.85) mm and coarse (0.85-4.0) mm aggregates using a mechanical sieve. The different aggregates were thoroughly washed with distilled water and oven dried. A foamseal ply board was machined into specific sizes of $100 \text{ mm} \times 100 \text{ mm} \times 100 \text{ mm}$ and assembled to complete 46 mortar box frames as shown in Fig. 2a. A hole was drilled in the centre on one side of the box (Fig. 2b) to make provision for 80 mm L-shaped deformed rebars to be inserted.

Portland cement Type 1, acquired from a local supplier, with the physical and chemical requirements meeting the ASTM C150-04a [16] standards was used. Cement, water and sand were mixed according to the industry standard ratio of 1:2:2.5, respectively. This ratio was adapted from Pacific Cement Limited, the commercial supplier of the cement.

The concrete blocks were cast by placing the fresh mortars in the wooden boxes and compacted by tapping on the sides of the box with a plastic mallet as recommended in the ASTM C192/C192M-06 [17] standard. This was necessary to minimise voids created by the air pockets. All concrete blocks were cured for 21 days under standard temperature and pressure conditions. After the curing process, the blocks were demoulded and the exposed L-shaped rebar was covered with an insulating tubing. 15 mortar blocks out of 46 blocks used were categorised as 'Main blocks' [M] while the remaining 30 were divided into two sets, marked as 'Reproducibility 1' and 'Reproducibility 2', [R1] and [R2] respectively. The last block was dedicated as a control specimen.

2.3. Electrochemical measurements

2.3.1. Galvanostatic pulse technique

The interfacial properties at the concrete/rebar interface were assessed using the short galvanostatic pulse technique (GPT) as illustrated in Fig. 3. The counter electrode used was a mild-steel plate, machined with hole in the centre as a provision for reference electrode insertion. The surface of the mild-steel was well polished to remove impurities.

Contact impedance between the counter electrode and the concrete surfaces were reduced using sponge soaked in respective salt solutions. National Instruments (NI) current (NI 9265) and voltage (NI 9215) modules, interfaced to the NI



Fig. 3. The three-electrode setup was used for short galvanostatic pulse measurements. Application of current stimuli and measurement of potential responses were conducted using National Instruments hardware.



Fig. 2. Schematic of a) complete box frame with inner dimension of 100 mm \times 100 mm \times 100 mm and b) cross-section of the cast box with rebar.

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