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

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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 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 \( R_o \) [8–12] as shown in Fig. 1.
The non-ideality in current ($A$), parameters ($R_p$), 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 foam seal ply board was machined into specific sizes of 100 mm × 100 mm × 100 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 1:2:5, 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 measurement. Application of current stimuli and measurement of potential responses were conducted using National Instruments hardware.

![Fig. 3](image3.png)
cDAQ-9174 chassis were used to provide short (1 s) galvanostatic pulses and simultaneously record the potential-time responses. To reduce noise, common grounds (COM) of both modules were connected together.

Each concrete blocks were submerged in the different electrolytes for the duration of the study and their open-circuit potentials were monitored continuously. The first set of GPT measurement was carried out after one week of immersion. For all measurements, the working electrodes were cathodically polarised to ensure minimal artificial damage to the rebars. The GPT measurements were conducted every seven days over a four-month period. Exposure conditions were varied during the time of measurement, which is explained as follows. Measurements carried out in first 4 weeks (Phase I) ensured that the concrete mortar blocks were removed out of the electrolytes and kept wet during measurements. At the end of weeks 5–7 (Phase II), measurements were conducted for the submerged concrete blocks. For Phase III (weeks 8–17) measurements, the blocks were partially dried a day ahead prior to GPT. This approach was aimed to investigate any significant variabilities in the measurements emanating from different conditions. Each measurement was replicated three times to ensure reproducibility and the repeated measurements were used to determine the weighted means and standard deviations [15,18] of the corrosion related parameters ($R_p$, $C_{dl}$, and $\beta$).

3. Results and discussion

3.1. Galvanostatic pulse measurements

Variations observed for the extracted corrosion parameters for the concrete mortar specimens immersed in five different concentrations of KCl, NaCl and MgCl$_2$ are presented. Before commencing with the discussion, it is of importance to highlight few aspects. In the present study, all specimens were exposed to chloride solutions for 17 weeks (120 days), thus some variations as an indication of corrosion is expected. With concrete cover of 46 mm, very minimal sorption of chlorides at rebar surface is anticipated. Following discussions will attempt to follow how $R_p$ vary at early stages, in varying chloride solutions.

3.1.1. Effects of chlorides on $R_p$, $C_{dl}$ and $\beta$-parameter

The analysed data in Fig. 4 illustrates $R_p$ values with a steady increase from first week in Phase I, which peaked in week 13 (Phase III) and gradually decreased. The observation from Phase I till midway of Phase III was expected since the time required for the chlorides to accumulate and initiate corrosion indicated rebar in passive state [19–21]. This indicated that ~90 days of submersion is essential for sufficient chloride to reach the rebar surface. However, reduction in $R_p$ after week 13 indicated active corrosion due to minimal build-up of chlorides at the steel rebar surface. Thus, as chloride concentrations increased at the steel-concrete interface, the passive layer continued to be reduced thereby reduction in $R_p$ trend. Nevertheless, under the influence of immersion duration, escalation of chlorides at the steel-concrete surface led

![Fig. 4](image-url)
to the slight increase in $R_p$, indicating development of temporary oxide layer.

Moreover, general reduction in $R_p$ due to increase in chloride concentration was generally well observed, particularly results in 0.01 M (Fig. 4a) and 0.1 M (Fig. 4d) which displayed strong influence on $R_p$ with increasing concentrations. The presence of this behaviour in $R_p$ possibly indicates increasing molarity of chlorides with increasing concentration has most likely accumulated the rebar surface with more chlorides, thus intensified during the breakdown of the passive layer and influencing corrosion rate as inferred from $R_p$. Hence, as the concentration increased the molarity of the salt increased simultaneously increasing the corrosion process and decreasing the $R_p$ mostly after week 12 to week 13.

Song et al. [22] highlighted that cations associated with less chloride (e.g., NaCl) is expected to have less binding capacity compared to those associated with large number of anions (e.g., MgCl$_2$). From Fig. 4, it is reflected that lowest $R_p$ was exhibited by NaCl, followed by KCl and then MgCl$_2$. This indicated that once ionic species were transported into the concrete, the distribution of the cations and anions accumulating at the rebar surface were influenced by its ionic sizes. It is reflective of the dissociation process of MgCl$_2$ which produced twice as much Cl$^-$ than magnesium ion (Mg$^{2+}$), exhibiting higher binding capacity which results in large $R_p$ compared to other two salts. The results for 0.06 M, 0.1 M and 0.15 M in Phase III indicates that smaller size of Mg$^{2+}$ enabled sufficient Cl$^-$ to diffuse and accumulate influencing corrosion, as inferred by lower $R_p$ measurements from week 12 to week 13.

The smaller ionic radii of sodium ion (Na$^+$) with lower binding capacity of chloride conceivably allowed more Cl$^-$ to diffuse and accumulate influencing corrosion, as inferred by lower $R_p$ measurements from week 12 to week 13. Also, the distinct observation for 0.06 M (Fig. 4c) of NaCl, suggested initiation of active corrosion at very early stage. Close observation of the $R_p$ trends demonstrated that breakdown in the passive layer occurred from week 9 to week 10. Furthermore, it is argued that large ionic radii of potassium ion (K$^+$) with chloride binding capacity similar to NaCl (less content of free Cl$^-$) significantly impeded Cl$^-$ from direct contact with rebar, thus resulting $R_p$ in between MgCl$_2$ and NaCl.

The analysed data in Fig. 5 illustrates $C_{dl}$ values with general reduction from first week in Phase I extending until Phase III. In

![Fig. 5](image)

*Fig. 5.* The $C_{dl}$ values for different concentrations of all salts at each phase and for control (distilled water) during different phases. *Note:* the error bars are significantly small.
comparison with $R_p$ trends in Fig. 4, an inverse relationship is observed between the two variables, reminiscent of the typical inverse relationship as emphasised in Birbilis et al. [13] and González et al. [23].

Birbilis et al. [13] have shown that the $\beta$-parameter may be an index to the distribution of active and passive sites upon corroding steel in a concrete environment. In the present work, variations in the observed trend of $\beta$ are illustrated in Fig. 6. The lower $\beta$ values

Fig. 6. The $\beta$ values of all three salts and for distilled water.

Fig. 7. Variation between corrosion potential, $E_{corr}$, and polarisation resistance $R_p$. 
in the range of 0.35–0.45 of all salt concentrations in the first week suggests passive state of rebar in the absence of chlorides. However, slight variations close to $\beta \approx 0.6$ observed in Phase III indicates presence of chloride, influencing corrosion. These observations further provide physical justifications to the observed trends of $R_p$ and $C_{dl}$ in Figs. 4 and 5. The error bars observed in Fig. 6 corresponds to standard deviation which was computed from the three sets of repeated measurements. Furthermore, this suggests
3.1.2. Relationship between corrosion potential $E_{corr}$ and $R_p$

Variations in $E_{corr}$ with $R_p$ for all the measurements over the 17-week period are illustrated in Fig. 7.

The purpose of this exercise was to observe the generated trends for each salt with respect to their polarisation resistance and corrosion potential. A strong relationship between $E_{corr}$ and $R_p$ indicates $E_{corr}$ becomes more positive as the $R_p$ increases. This was an important characteristic of all the measurements since the relationship exhibited by these two parameters confirmed the absence of diffusion effects in the system [15, a justification that $R_p$ can be safely ignored in the present work.

3.2. Evaluation of cation influence

In order to develop some formative conclusions on the influence of cations as motivated in the present work, a normalisation procedure was necessary. This was achieved with a normalisation index (N.I.), whereby the corrosion related parameters in different salt concentrations were compared with that to a reference concentration of 0.01 M of the same salt. The 0.01 M was chosen based on its minor molarity, thus facilitated comparison with other concentrations in terms of corrosion degree. To obtain N.I., all $R_p$ and $C_{dl}$ values obtained for each salt at different concentrations were compared with $R_p$ and $C_{dl}$ of 0.01 M, respectively.

The variations in normalised $R_p$ ($R_p^{(Norm)}$) and $C_{dl}$ ($C_{dl}^{(Norm)}$) values for 0.03 M, 0.06 M, 0.1 M and 0.15 M (Fig. 8) and the summary values (Table 1) were computed through principle of weighted means and standard deviations.

From Fig. 8 and Table 1, majority of $R_p^{(Norm)}$ values displayed reduction in $R_p$ when compared with 0.01 M while $C_{dl}^{(Norm)}$ values increased, reminiscent of their inverse relationship [23]. The chloride effect on the $R_p^{(Norm)}$ and $C_{dl}^{(Norm)}$ of KCl initially absent in the first few weeks apparently manifested around week 11 to week 12. The $R_p$ trends of MgCl₂ before and after normalisation suggested strong protection of rebar. Similarly, disturbance in the protection layer in all normalised concentrations was seen to vary during week 11 to week 12, correlating with the observations made before normalisation.

A good agreement is observed between the $R_p^{(Norm)}$ trends of NaCl in all concentrations and Table 1. Further observations revealed that the majority of values appearing close to lower $R_p^{(Norm)}$ were between week 10 to week 12. The weak fluctuations of $R_p^{(Norm)}$ observed after week 13 to week 14 in all concentrations is possible indications of the dynamics of oxide layer. Although the chloride escalation time in 0.03 M (Fig. 8a) and 0.15 M (Fig. 8d) appears similar, significant fluctuations as a result of cyclic reaction is seen to feature in 0.15 M after week 11. This characteristic appears to reflect the obvious notion that higher concentrations leads to strong chloride influence. Moreover, the distinct observation made for 0.06 M of NaCl (Fig. 4) is also observed for $R_p^{(Norm)}$ in Fig. 8 where variation in the trend is observed mostly after week 11.

To develop an understanding of these observations, a discussion on the diffusivity of ionic species in concretes is necessary. Samson et al. [24] emphasised that movement of ions in porous materials occur in the liquid phase as result of complex interaction within the material. The diffusion coefficient, $D_e^0$ of the ionic species in free water that are mostly found in cement based materials is presented in Table 2.

In line with Song et al. [22], K⁺ and Na⁺ are suggested to occupy the steel-concrete interface since both ions are diffusible (Table 2). However, the binding capacity of Cl⁻ inflicted slower diffusion rate of K⁺, impeding the corrosion of rebar. This explains the observation of decreasing $R_p^{(Norm)}$ with increasing concentration (Table 1). However, for 0.15 M (Table 1), the $R_p^{(Norm)}$ values have increased due to relatively large maximum $R_p$ (Fig. 4) during week 12 compared to other concentrations. For NaCl arrangement, Na⁺ with lower binding capacity has allowed build-up of Cl⁻ at the rebar surface, hence influencing corrosion. This explains the observed $R_p^{(Norm)}$ trend after week 12 to week 13. The distinct observation made for 0.06 M (Fig. 8b) probably suggests accumulation of Cl⁻ at the rebar surface prior to week 12, thus resulting in early breakdown of the passivated layer. However, it continued to remain in lower region of $R_p^{(Norm)}$. For observations in MgCl₂, it must be emphasised from earlier discussions that higher $R_p^{(Norm)}$ values were mainly due to presence of the two chloride ions, thus inflicting higher chloride binding capacity. Hence, the rebar surface appeared to be occupied with less amount of free chloride ions, influencing lesser degree of corrosion compared to NaCl and KCl.

4. Conclusion

Application of the short galvanostatic pulse technique in this study has facilitated in evaluating the early stages of corrosion through characterisation of the steel-concrete interface. The study has identified that in the absence of chlorides, rebars are mostly protected by the passivated layer. Increasing concentrations of chlorides suggested greater extent of induced corrosion. It was found that corrosion rate of different salts in different solutions varied, albeit all three salts had chlorides in common. It was inferred that cations also have probable influence during rebar corrosion. The normalisation framework utilised in the present work aided in evaluating the corrosion parameters. Similarities in the corrosion intensities before and after normalisation procedure indicated that the framework is sound. An assessment of the nor-

### Table 1

<table>
<thead>
<tr>
<th>Salt Concentrations</th>
<th>0.03 M</th>
<th>0.06 M</th>
<th>0.1 M</th>
<th>0.15 M</th>
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<tbody>
<tr>
<td>$R_p^{(Norm)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>0.75 ± 0.02</td>
<td>0.66 ± 0.01</td>
<td>0.558 ± 0.001</td>
<td>0.75 ± 0.01</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>1.08 ± 0.04</td>
<td>0.335 ± 0.001</td>
<td>0.354 ± 0.001</td>
<td>0.391 ± 0.001</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.101 ± 0.001</td>
<td>0.237 ± 0.001</td>
<td>0.368 ± 0.001</td>
<td>0.944 ± 0.001</td>
</tr>
<tr>
<td>$C_{dl}^{(Norm)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>1.4 ± 0.1</td>
<td>1.10 ± 0.01</td>
<td>1.12 ± 0.01</td>
<td>1.16 ± 0.02</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.555 ± 0.001</td>
<td>1.0 ± 0.1</td>
<td>0.088 ± 0.001</td>
<td>0.514 ± 0.003</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.233 ± 0.001</td>
<td>2.0 ± 0.2</td>
<td>2.3 ± 0.1</td>
<td>2.22 ± 0.01</td>
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</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Ions</th>
<th>$D_e^0$ ($10^{-9}$ m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>1.33</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.555 ± 0.001</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.233 ± 0.001</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.03</td>
</tr>
</tbody>
</table>
malised $R_p$ and $C_{ll}$ trends indicates that NaCl solutions are more corrosive than MgCl$_2$ and KCl. This feature needs further investigation as it will lead to a deeper understanding of the corrosion processes in the natural environment.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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References