

Short Communication

Effect of Chlorine Diffusion on Corrosion Activity of Mild Steel-Concrete in Malaysian Seawater

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ABSTRACT: This study investigated the chloride diffusion through cement mortar and corrosion of mild steel in mortar. The chloride diffusion profile was observed in three stages: non-steady, transition, and steady states. The open-circuit potential (OCP) properties of mild steel were related to the chloride diffusion profile. The OCP value did not change considerably in the non-steady state, continuously decreased in the transition state, and stabilized in the steady-state diffusion. Corrosion measurement was terminated at a stable OCP value of -0.600 V.

Keywords: Malaysian sea water; Salinity; Open-circuit potential; Corrosion

1. Introduction

Concrete is the most widely used construction material and is always reinforced by steel bars for improved mechanical properties. Unreinforced concrete is a brittle material possessing low tensile strength and low strain capacity [1]. In Malaysia, concrete is used for the construction of bridges, offshore oil and gas production platforms, and onshore buildings.

The mild steel reinforcement in concrete is normally protected by the formation of a passive film caused by the generation of $\text{Ca}(\text{OH})_2$ from the hydration of cement [2]. However, this passive film is subject to breakdown when exposed to seawater. Chloride in seawater can penetrate into the concrete and initiate damage to the passive film.

When the breakdown begins, the metallic substrate with low oxygen concentration is oxidized, and oxygen reduction occurs in the area with high oxygen concentration. This redox reaction leads to the corrosion of mild steel in concrete. The reversion of calcium hydroxide to calcium carbonate may lead to insufficient alkalinity to support passivation, which facilitates chloride attack. When the reinforcing steel bars corrode, the concrete material deteriorates. This occurrence subjects the concrete to additional expansive pressures, which causes cracking, spalling, and delamination of the concrete cover [3].

The half-cell method is the most common method used to measure corrosion activity [4]. This technique evaluates the open-circuit potential (OCP) of mild steel. The OCP value provides information on the corrosion probability only. Numerous studies were conducted on the corrosion of concrete by using different seawater or artificial seawater with 3.5% NaCl. Nonetheless, Malaysian seawater is rarely used. Thus, the objective of this study is

to observe the effect of chloride ion penetration into concrete toward the corrosion of mild steel using Malaysian seawater.

2. Experimental

2.1 Raw Material Characterization

Ordinary Portland cement (OPC, Blue Lion Cement, Malaysia) was analyzed with X-ray fluorescence (XRF) for chemical composition identification. Sand was washed with water to remove the water-soluble contaminants and dried in an oven at 110°C for 24 h. The sand used was characterized with a dry particle size analyzer by Sympatec.

2.2 Mortar Slab Preparation

Mortar paste was prepared using OPC Portland Cement CEM Type I. The water-cement and cement-sand ratios were 0.60 and 1:3, respectively. Cement was mixed homogeneously with water, and sand was added after mixing. The well mixed mortar paste was placed into a compact polyvinyl chloride mold (with a diameter of 110 mm and a thickness of 10 mm). The mortar was dried under a normal room condition for 2 days.

2.3 Slab Porosity Measurement

Porosity test was made using Archimedes' method. The mortar slab that was cured for 2 days, dried in an oven at 110 °C for 24 h and then weighed. The mortar was then immersed in distilled water and vacuumed for 3 h, weighed again while suspended in the distilled water, and then removed from the distilled water. The vacuum wet weight of the mortar slab was measured immediately. The apparent porosity was calculated based on the Equation (1):

$$\text{Porosity (\%)} = \frac{W-D}{W-S} \times 100\% \quad (1)$$

where W is the water saturated weight, D is the dry weight, and S is the suspended weight.

2.4 Open-circuit Potential

A mild steel rod 15 mm in diameter was cut into a pellet form 5 mm in thickness. The pellet was connected to a wire and mounted with epoxy. The sample surface of the mild steel was ground with a silicon carbide paper.

The OCP measurement setup is presented in Figure 1. The mortar slab was placed between two acrylic chambers (600 ml each). The catholyte chamber was filled with seawater, whereas the anolyte chamber was filled with deionized (DI) water. The seawater (3.0‰) was obtained near Pulau Langkawi, Kedah, Malaysia.

A potential of 6.0 V was applied to diffuse the chloride ion. The mounted mild steel was placed inside the anolyte chamber with the saturated calomel electrode (SCE) and connected to a multimeter. For the control sample, in another cell, the mounted mild steel pellet was immersed directly into the seawater with SCE as the reference electrode. The salinity of the anolyte was measured with an Omega CDH45 meter. The OCP measurement was also determined.

3. Results and discussion

3.1 Characterization of Materials

The maximum size of the sand particles was 0.294 mm, and the mean value was approximately 0.164 mm. According to American Society for Testing and Materials (ASTM) C136, an aggregate qualifies as fine aggregate when the aggregate particles pass a 4.75 mm sieve but retain on a 75 µm sieve, thus, the sand used in this study is a fine aggregate. This standard is consistent with Malaysian Standard.

Table 1 presents the chemical composition of the cement identified by XRF analysis. The main constituent of OPC was CaO, followed by SiO₂, Al₂O₃, SO₃, and Fe₂O₃. These five chemical compounds are the major constituents of a cement clinker with 96.78 wt%. According to the European standard, cement contains at least 95 wt% of clinker; thus, the cement material with 96.78 wt% of clinker used in this study is verified as an OPC CEM I.

The calculated apparent porosity of mortar slabs was calculated at 13.27%. Lafhaj et al. [5] verified the porosity of slabs at 13.50% by using the water–cement ratio of 0.60. Increasing the water–cement ratio will increase the porosity of the hardened cement.

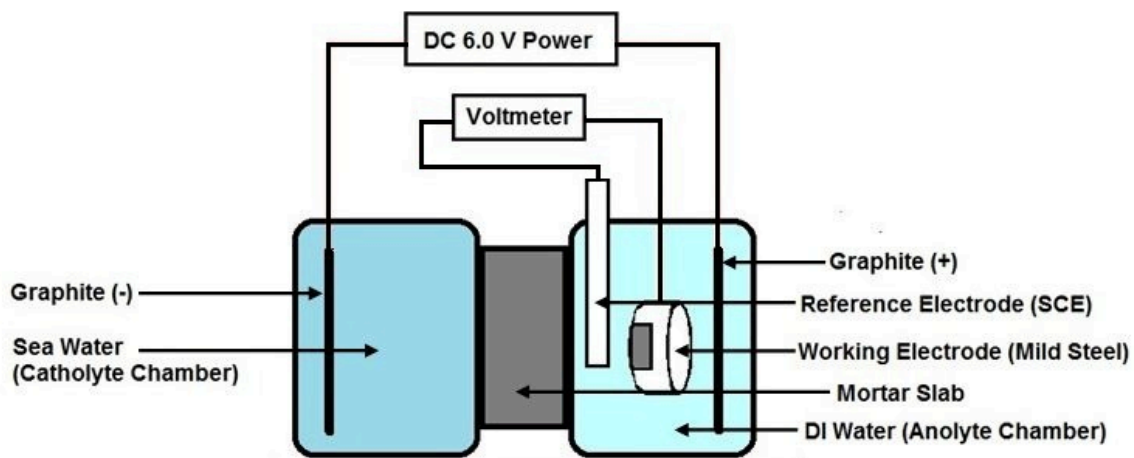


Figure 1: Schematic setup of corrosion cell for salinity and open-circuit potential measurement

Table 1: Chemical Compositions of Ordinary Portland Cement (CEM Type I) by XRF Analysis

Chemical Content (wt%)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂
	0.05	1.13	5.46	21.95	0.07	5.36	1.20	60.18	0.24
Chemical Content (wt%)	Cr ₂ O ₃	MnO	Fe ₂ O ₃	NiO	ZnO	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂
	0.06	0.20	3.83	0.01	0.01	0.01	0.01	0.05	0.01

* LOI = 0.16 wt%

Porosity measurement mainly determines the open pores in the mortar slabs. Permeability of a ceramic material is significantly affected by the open pores in the particular product. Permeability determines the ease of entry of fluid, gases, and vapor to the concrete material [6]. Porosity in the hardened cement paste is low when a lower water–cement ratio is used [7]. The apparent porosity of the mortar slabs was mostly constant in this study. The results indicated that the mortar slabs possess a uniform permeability. Salinity and OCP measurements were not affected by the differences in porosity.

3.2 Salinity Permeability

Figure 2 presents the salinity permeability from seawater to DI water. During 8 h of immersion, the salinity concentration was low. Salinity concentration increased slowly from 0.0% to 0.1% from 8 to 24 h of immersion. Then after 24 h, salinity concentration continuously increased with time. These three stages of diffusion are referred to as the non-steady state, transition state, and steady state, respectively [8].

In the non-steady state of diffusion, Cl⁻ started to penetrate and move through the mortar slabs. Chlorine had not reached the DI water in this state. The transition state occurred when Cl⁻ successfully penetrated into the DI water, as shown by the changes in salinity from 0.0% to 0.1%. Cl⁻ then began to move into the DI water. The steady state occurs when salinity increases proportionally with time. The fluxes of Cl⁻ penetrating the mortar slabs also become constant in this state [9].

3.3 Open-circuit Potential

Figure 3 shows the average OCP of mild steel in seawater for the control samples. The control samples rapidly decreased within 1 h of immersion and slowly decreased after 3 h. The OCP showed that the mild steel is corroding after the first hour of immersion in seawater. The samples then stabilized at -0.712 (vs. SCE) V after 7 h. This behavior is similar to the OCP measured with an unmodified coating for steel in the study by Martyak and McAndrew [10].

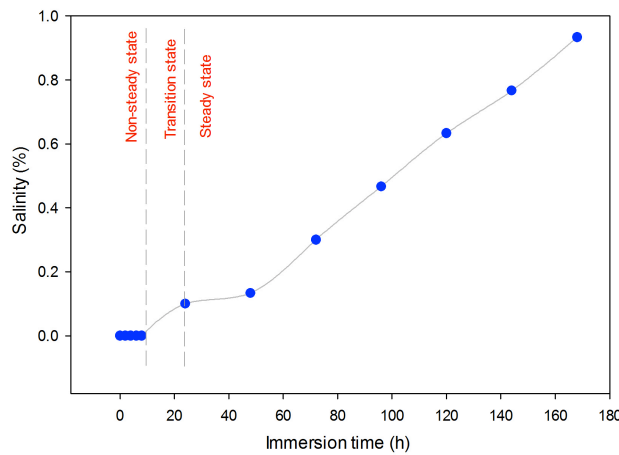


Figure 2: Salinity in the analyte of deionized water for the corrosion cell

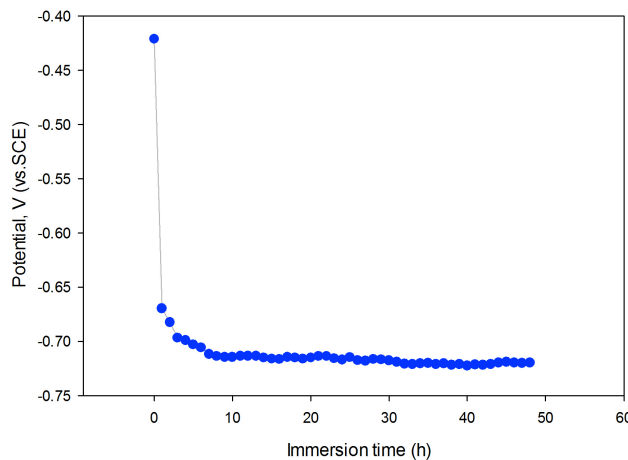


Figure 3: Open-circuit potential for mild steel immersed in seawater

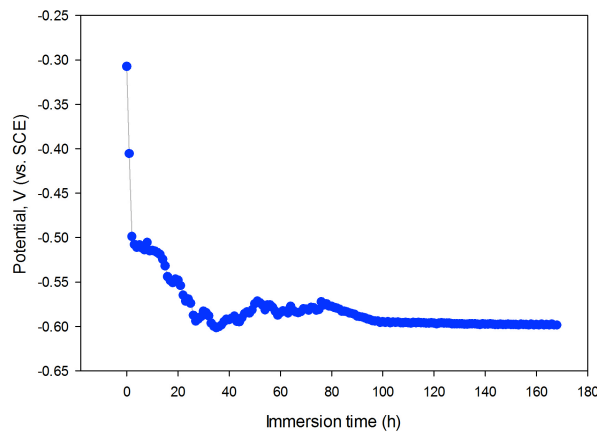


Figure 4: Open-circuit potential for mild steel immersed in the anolyte of corrosion cell

Figure 4 presents the average OCP of mild steel measured with a corrosion cell. The OCP fluctuated from the beginning until 78 h of immersion and then stabilized at -0.600 V (vs. SCE). The comparison of the OCP reduction between the control samples and the corrosion cell samples indicates that the OCP reduction rate was higher in direct immersion in seawater. Yu et al. [11] claims that the potential continuously drops below -0.200 V (vs. SCE) when a threshold of Cl^- is reached. The reduction in OCP of the mild steel samples indicated the initiation of corrosion on the mild steel. The probability of corrosion is higher than 95% when the OCP is more than -0.270 V (vs. SCE) [12].

Fluctuation in OCP is normally contributed by passivation and de-passivation that occurred on the mild steel [13]. The OCP increased during passivation, and vice versa during de-passivation. The OCP fluctuated along the OCP testing; however, such fluctuation occurred in a small range. The plot depicting the OCP is almost a flat line in the stable state. The OCP reduction in the corrosion cell was also following the three diffusion states: non-steady, transition, and steady. The rapid decrease in the non-steady state could be a reaction to the insufficient amount of Cl^- ; however, the OCP did not change significantly when it reached -0.500 V (vs. SCE). The OCP decreased and then fluctuated in the transition state. The fluctuation could be due to the insufficiency of Cl^- in DI water for the formation of initiation of de-passivation. The increase of Cl^- concentration in the DI water caused the solution to become more aggressive. OCP decreased continuously in the steady state.

4. Conclusion

The OCP shows that the corrosion activity on mild steel is affected by the Cl^- diffusion profiles. Chlorine diffusion through mortar or concrete occurs in three states: non-steady, transition, and steady. The OCP changes according to these three states of the diffusion profile. The more aggressive state is the transition state in which the Cl^- successfully penetrates the mortar.

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References

1. A.A. Shah, Y. Ribakov, Mater. Des. 32 (2011) 4122-4151.
2. H.-W. Song, S.-W. Pack, K.Y. Ann, Constr. Build. Mater. 23 (2009) 3270-3278.
3. L. Chernin, D.V. Val, Constr. Build. Mater. 25 (2011) 1854-1869.
4. R. Huang, C.C. Yang, Cem. Concr. Compos. 19 (1997) 131-137.
5. Z. Lafhaj, M. Goueygou, A. Djerbi, M. Kaczmarek, Cem. Concr. Res. 36 (2006) 625-633.
6. E.P. Kearsley, P.J. Wainwright, Cem. Concr. Res. 31 (2001) 805-812.
7. A. Dureković, Cem. Concr. Res. 25 (1995) 365-375.
8. C.C. Yang, S.C. Chiang, L.C. Wang, Constr. Build. Mater. 21 (2007) 1560-1567.
9. C.C. Yang, Cem. Concr. Res. 36 (2006) 1304-1311.
10. N.M. Martyak, P. McAndrew, Corrosion Sci. 49 (2007) 3826-3837.
11. H. Yu, K.-T.K. Chiang, L. Yang, Constr. Build. Mater. 26 (2012) 723-729.
12. T.-P. Cheng, J.-T. Lee, W.-T. Tsai, Cem. Concr. Res. 20 (1990) 243-252.
13. M. Saremi, E. Mahallati, Cem. Concr. Res. 32 (2002) 1915-1921.

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